ENVIRONMENTAL RESEARCH

TECHNOLOGY TRANSFER CONFERENCE

ISSN 0825-4591

Ontario

Environment
Environnement

Jim Bradley, Minister/ministre

PROCEEDINGS

VOLUME I
FEATURE PRESENTATIONS
AIR QUALITY RESEARCH
WATER QUALITY RESEARCH

A Decade of Sharing Results

November 20 & 21, 1989
Royal York Hotel
Toronto, Ontario
Canada

Environment Ontario WE RECYCLE

Cover Printed on Recycled Paper

ISSN 0825-4591

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VOLUME I

FEATURE PRESENTATIONS
AIR QUALITY RESEARCH
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Sponsored by
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Introduction

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario Universities and by private research organizations and companies.

The papers presented at the Environmental Research: 1989 Technology Transfer Conference are published in two volumes of conference Proceedings corresponding to the following sessions:

VOLUME I: FEATURE PRESENTATIONS
AIR QUALITY RESEARCH
WATER QUALITY RESEARCH

VOLUME II: LIQUID & SOLID WASTE RESEARCH
ANALYTICAL METHODS
ENVIRONMENTAL SOCIO-ECONOMICS

Volume I is comprised of presentations given during Session A and Session B of the conference, as well as all Feature Presentations.

For references purposes, indices for all sessions may be found at the front of both volumes.

For further information on any of the papers, please contact either the authors or the Research and Technology Branch at (416) 323-4574 or 323-4573.

Acknowledgments

The Conference Committee would like to thank the authors for their valuable contributions to environmental research in Ontario.

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VOLUME I

INDEX

Feature Presenters **Page**

Air Quality Research

A1 **Dealing with Climate Change: The Agenda for the Next Decade;** H. Hengeveld, Atmospheric Environment Service, Environment Canada, Downsview, Ontario. 1

A12 **Recent Developments in Applied Dispersion Modelling;** J. Weil, Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, Colorado, U.S.A. 20

Water Quality Research

B1 **Lessons Learned from 20 Years of Experimental Manipulations at the Experimental Lakes Area;** R. Hesslein, Freshwater Institute, Winnipeg, Manitoba. 5

B12 **International Perspectives on Drinking Water Research;** F. Fiessinger, Past Chairman, International Water Supply Association, currently, Zenon Environmental Inc., Burlington, Ontario. 27

Liquid & Solid Waste Research

C1 **Diffusion Profiles in Barrier Clays: Laboratory and Field Experiences;** R. Quigley, The University of Western Ontario, London, Ontario. 9

C12 **The Solid Waste Issue: The Plastics Industry's Initiatives;** M. Hyde, DOW Chemical Canada Inc., on behalf of The Environment and Plastics Institute of Canada, Toronto, Ontario. 30

Analytical Methods Research

D1 **Application of Inductively Coupled Plasma Mass Spectroscopy for the Analysis of Marine Reference Materials;** J. McLaren, National Research Council, Ottawa, Ontario. 13

D12 **Ambient Pressure Ionization Methods for Environmental Analysis;** H.J. Hill, Department of Chemistry, Washington State University, Pullman, Washington, U.S.A. 32

Environmental Socio-Economics

E1 **Towards a Better Integration of Environmental, Economic and Other Governmental Policies;** M. Potier, Division Chief, Environment and Economics, O.E.C.D., Paris, France 17

E12 **Economic Evaluation of Global Warming Policies;** D.N. Dewees, Department of Economics, University of Toronto, Toronto, Ontario. 36

VOLUME I

SESSION A: AIR QUALITY RESEARCH

Verbal Presentations **Page**

A2 **Chemical Transformation of a Pollutant in the Troposphere by Competing Pathways: Photolysis by Sunlight and Hydroxyl Radical Attack**; N.J. Bunce*, J.S. Nakai and M. Yawching, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario. 49

A3 **Ambient Air Analysis with a Thermal Desorption Gas Chromatograph/Matrix/Isolation/Infrared Spectrometer System**; R.E. Chapman, Air Resources Branch, Environment Ontario, Toronto, Ontario. 57

A4 **Development of Ambient Air Monitoring Methodologies for Dioxins and Furans**; R. Clement*, P. Steer, C. Tashiro and M. Lusis, Environment Ontario, Toronto, Ontario, and T. Dann, C. Chiu and M. Bumbaco, Environment Canada, Ottawa, Ontario. 67

A5 **Method Development and Evaluation for the Monitoring and Analysis of Odorous Organics in Ambient Air**; P. Forsythe*, C. Chan, L. Vainer and J. Martin, Mann Testing Laboratories Limited, and B. Foster and P. Steer, Environment Ontario, Toronto, Ontario. 75

A6 **Atmospheric Trace Gas Measurements Using a Tunable Diode Laser Absorption Spectrometer**; D.R. Hastie*, R. Berman and H.I. Schiff, Department of Chemistry and Centre for Atmospheric Chemistry, York University, North York, Ontario. 85

A7 **Atmospheric Measurements of Natural Hydrocarbons Using Gas Chromatography/Mass Spectrometry;** H. Niki* and B.H. Khouw, Chemistry Department and Centre for Atmospheric Chemistry, York University, North York, Ontario. 94

A8 **Multiple Option Approach to the Risk Assessment for Mixtures (Experience with PAH);** P. Muller* and B. Leece, Hazardous Contaminants Coordination Branch, Environment Ontario, Toronto, Ontario. 102

A9 **Dose Response for Selected Environmental Air Pollutants: Results from a Study on Runners;** F. Silverman*, R.B. Urch, P. Corey and R.J. Shephard, The Gage Research Institute, Toronto, Ontario. 124

A10 **Investigation of Short-Term Mutagenicity & Chemical Composition of Organic Solvent Extractable Fraction of Coke Oven Emission;** A.J. Horton*, N. Belson, K. Shaw, J. Beetham and G.H. Thomas, ORTECH International, Sheridan Park Research Community, Mississauga, Ontario. 134

A11 **Genotoxic Compounds Associated with Respirable Urban Air Particulate – Chemical Fractionation and Bioassay of Complex Mixtures;** D.W. Bryant*, B.E. McCarry and D.R. McCalla, Department of Biochemistry and Chemistry, McMaster University, Hamilton, Ontario. 138

A13 **Eulerian Model Evaluation;** M. Alvo, Department of Mathematics, University of Ottawa, Ottawa, Ontario. 148

A14 **Testing Atmospheric Dispersion Model Performance Using Air Pollution Data Sets from Chalk River and Sudbury;** E. Robertson* and P.J. Barry, Environmental Research Branch, Chalk River Nuclear Laboratories, Chalk River, Ontario. 154

A15 **Scale Model Studies and Development of Prediction Procedures for Heavy Gas Dispersion in Complex Terrain;** M.C. Murphy*, K.C. Heidorn, P.A. Irwin and A.E. Davies, Rowan Williams Davies & Irwin Inc., Guelph, Ontario. 162

A16 **Comparison of the Source Locations of Acidic Particles and Precipitation in Ontario;** Y. Zeng and P.K. Hopke*, Department of Chemistry, Clarkson University, Potsdam, New York and S.J. Yoon, Department of Civil Engineering, University of Illinois, Urbana, Illinois, U.S.A. 170

A17 **Impact of Ozone on Ontario Vegetation;** R.G. Pearson*, Air Resources Branch and J.A. Donnan, Policy and Planning Branch, Environment Ontario, Toronto, Ontario. 178

A18 **Carbohydrate and Micronutrient Profile of Sap in Healthy and Declining Sugar Maple Trees in Ontario;** S.N. Pathak*, and D.N. Roy, University of Toronto, Toronto, Ontario. 185

VOLUME I

SESSION A: AIR QUALITY RESEARCH

Poster Presentations

		Page
AP1	**Establishing Vegetation on Erosion-Prone Landfill Slopes in Ontario;** T.W. Hilditch, A.J. Gould and N. DeFraeye, Gartner Lee Limited, Markham, Ontario.	193
AP2	**Source Identification and Apportionment for Airborne Particles in Hamilton, Ontario;** Y. Zeng and P.K. Hopke, Clarkson University, Potsdam, N.Y., U.S.A. and D. Wang, University of Illinois, Urbana, Illinois, U.S.A.	194
AP3	**A Year Experience with the Air Quality Index System in Ontario;** D. Yap, Air Resources Branch, Environment Ontario, Toronto, Ontario and D. Mignacca and D. Fraser, KelResearch Corporation, Downsview, Ontario.	210
AP4	**Risk Assessment with Complex Mixtures;** D.M. Logan and A. Raj, Biology Department, York University, North York, Ontario.	214
AP5	**Concurrent Detection of Gene Mutations and Chromosomal Aberrations Induced *In Vivo* in Somatic Cells;** J.A. Heddle, A. Bouch, M. Khan and J.D. Gingerich, Department of Biology, York University, North York, Ontario.	218

AP6 **Optical Configurations for Efficient Collection of Fluorescent Radiation from Chemically-Selective Lipid Monolayers and Multilayers;** U.J. Krull, R.S. Brown, S. Ferraro and M. Heimlich, Department of Chemistry, Erindale College, University of Toronto, Mississauga, Ontario. 223

AP7 **Atmospheric Deposition of Chlorinated Organic Compounds in the Great Lakes Basin;** M.N. Shackleton, D.B. Orr and N.W. Reid, Air Resources Branch, Environment Ontario, Toronto, Ontario. 227

AP8 **Ignition Studies of Selected Explosive Mixtures of Gases and Dusts Emitted from Cement Kilns;** I.I. Inculet, G.S.P. Castle, E.J. Weckman, K.A. Shelstad and M.L. Wick, The University of Western Ontario, London, Ontario. 232

AP9 **On Two-Phase Flow Modeling of Wind-Induced Particle Erosion Rates within a Turbulent Boundary Layer;** A.D. Ciccone, J.G. Kawall and J.F. Keffer, University of Toronto, Toronto, Ontario. 236

AP10 **Growth Effects of Naphthalene and Naphthal on Plants: The Role of Soil Type in Modification of Tomato, Radish and Swiss Chard Responses;** B.A. Marie and D.P. Ormrod, Department of Horticultural Sciences, University of Guelph, Guelph, Ontario. 240

AP11 **A Method of Integration for Gas-Phase Air Chemistry Models;** H.R. Cho and P. Makar, Department of Physics, University of Toronto, Toronto, Ontario. 244

AP12 **Microwave Induced Catalytic Destruction of Some Gaseous Air Pollutants;** M.C. Depew and J.K.S. Wan, Department of Chemistry, Queen's University, Kingston, Ontario. 247

AP13 **An Investigation of Vibration Isolation in a House for Reduction of Train Vibrations;** J.H. Rainer, M.O. Al-Hunaidi and G. Pernica, Institute for Research in Construction, National Research Council of Canada, Ottawa, Ontario. 251

AP14 **Adaption of a Mesoscale Model to Study Air Pollution in the Toronto area;** M. Niewdomski, Department of Physics, University of Toronto, Toronto, Ontario. 254

VOLUME I

SESSION B: WATER QUALITY RESEARCH

Verbal Presentations **Page**

B2 **Organic Contaminants in Food Webs; Mechanisms, Models and Management;** F. Gobas* and G.D. Haffner, Great Lakes Institute, University of Windsor, Windsor, Ontario. 257

B3 **Organochlorine Contaminant Burdens of Adult Aquatic Insects Collected from Great Lakes Connecting Channels;** Z.E. Kovats* and J.H. Ciborowski, Department of Biological Sciences, University of Windsor, Windsor, Ontario. 267

B4 **Contaminants in Ontario Sport Fish – Long Term Trends and Future Prospects;** A.F. Johnson*, C.M. Cox and A.L. Vaillancourt, Water Resources Branch, Environment Ontario, Toronto, Ontario. 285

B5 **Contaminants in Biota and Sediments in Shoreline Habitats of the Bay of Quinte, Lake Ontario;** A. Crowder*, W. Dushenko, J. Poland and J. Greig, Department of Biology and Chemistry, Queen's University, Kingston, Ontario. 292

B6 **Carcinogenicity Testing of Industrial Effluents Using a Rainbow Trout Bioassay;** C.D. Metcalfe, Trent University, Peterborough, Ontario. 302

B7 **Hepatic Metabolism of Benzo-a-Pyrene in White Suckers (*catostomus commersoni*) from Polluted and Reference Sites in the Great Lakes: Role of Glutathione S-Transferase;** G.M. Kirby*, J.R. Bend, H.W. Ferguson, I.R. Smith and M.A. Hayes, Department of Pathology, University of Guelph, Guelph, Ontario. 311

B8 **Use of Sphaeriidae Clams for Assessing the Toxicity of Contaminated Sediments;** G.L. Mackie, Department of Zoology; University of Guelph, Guelph, Ontario. 321

B9 **Residue-Based Interpretation of Toxicity and Bioconcentration QSARs Based on Aquatic Bioassays;** L.S. McCarty* and A.D. Smith, Biology Department, University of Waterloo, Waterloo, Ontario and G.W. Ozburn, Lakehead University, Thunder Bay, Ontario. 333

B10 **Development of a Water Quality Criterion for Thiocyanate in Ontario;** R.P. Lanno*, S.D. Kevan and D.G. Dixon, Department of Biology, University of Waterloo, Waterloo, Ontario. 341

B11 **The Use of Mass Balance Models to Elucidate the Effects of In-Place Pollution;** M.L. Diamond*, D. Mackay and W. Stiver, Institute for Environmental Studies, University of Toronto, Toronto, Ontario. 352

B13 **Reproductive Outcomes in Southwestern Ontario, 1980 to 1985;** J. McD. Robertson* and H.J. Chan, Department of Epidemiology and Biostatistics, The University of Western Ontario, London, Ontario. 359

B14 **Development and Pilot Scale Demonstration of a Powdered Activated Carbon/Ultrafiltration System for Drinking Water Treatment;** H. Donison*, A. Benedek and J.J. Bancsi, Zenon Environmental Inc., Burlington, Ontario. 367

B15 **Slow Sand Filtration – Pilot Plant Testing of Critical Questions in Drinking Water Production;** W.J. Hargrave, Water Division, Gore and Storrie Ltd., North York, Ontario. 376

B16 **Emerging Advanced Technology for Destruction of Waterborne Organic Pollutants;** H. Al-Ekabi*, A. Safarzadeh-Amiri and M. Robertson, Nulite, A Division of Nutech Energy Systems Inc., London, Ontario. 379

B17 **Hydrogeologic Model of De-Icing Salts in the Environment: A Salt Balance in an Urban Watershed;** J. Haynes* and K.W.F. Howard, Groundwater Research Group, University of Toronto, Scarborough Campus, Scarborough, Ontario. 390

B18 **Characterization of the Fecal Indicator Bacterial Flora of Sanitary Sewage with Application to Identifying the Presence of Sanitary Waste in Storm Sewers;** P. Seyfried and T. Bleier, Department of Microbiology, University of Toronto, Toronto, Ontario. 404

VOLUME I

SESSION B: WATER QUALITY RESEARCH

Poster Presentations

		Page
BP1	**Twelve-Mile Creek and Welland River. In Place Pollutant Report;** I.D. Brindle, B. Buchanan, X-F. Li, L.T. Pidwerbesky, Chemistry Department, Brock University, St. Catharines, Ontario.	408
BP2	**The Use of *Tradescantia* and *Vicia Faba* Bioassays for the *In Situ* Detection of Mutagens in an Aquatic Environment;** W.F. Grant, H.G. Lee, D.M. Logan, Department of Biology, York University, Downsview, Ontario and M.F. Salamone, Environment Ontario, Toronto, Ontario.	410
BP3	**Landsat-5 TM Spectral Responses for Lakes Across Northern Ontario;** J.R. Pitblado, D. Dempsey, P. Savard and T. Jetty, Geography Department, Laurentian University, Sudbury, Ontario.	411
BP4	**The Origin and Distribution of Methane in the Alliston Aquifer Complex, Southern Ontario;** R. Aravena, L. Wassenaar, J. Barker and R. Gillham, Institute for Groundwater Research, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario.	414

BP5 **Microbial Methylation of Mercury in Acid Stressed Lakes – Role of Sulphate Reducing Bacteria;** A. Kerry, BIOS Environmental Research, Toronto, Ontario, P.M. Stokes, Institute for Environmental Studies, University of Toronto, Toronto, Ontario, and B. Prucha and G. Mierle, Dorset Research Centre, Dorset, Ontario. 417

BP6 **Influence of Lake pH and Macrograzers on the Distribution and Abundance of Nuisance Metaphytic Algae in Central Ontario, Canada;** R. France and P. Stokes, Institute for Environmental Studies, University of Toronto, Toronto, Ontario. 420

BP7 **Assessment of Fecal Pollution Transport in Agriculturally Impacted Watersheds Using a Biotracer;** M. Walters, Lake Simcoe Region Conservation Authority, Newmarket, Ontario. 423

BP8 **Sediment Transport Model, Research and Implementation;** W.F. Hollarum and M.D. Palmer, Beak Consultants Ltd., Brampton, Ontario and R.J. Dewey, Gore and Storrie, Toronto, Ontario. 425

BP9 **In Situ Determination of Fecal Indicator Bacteria Survival in Agriculturally Impacted Watersheds;** E. Harris and M. Walters, Lake Simcoe Region Conservation Authority, Newmarket, Ontario. 426

BP10	**The Effects of Agricultural Drainage on Sediment and Water Quality Loadings;** J.D. Paine and W.E. Watt, Department of Civil Engineering, Queen's University, Kingston, Ontario.	429
BP11	**Trend Analysis Procedures for Water Quality Time Series;** A.I. McLeod, The University of Western Ontario, London, Ontario, and K.W. Hipel, University of Waterloo, Waterloo, Ontario, and B. Bodo, Environment Ontario, Toronto, Ontario.	432
BP12	**Greywater Disposal from Pleasure Boats;** M.F. Holloran and M.D. Palmer, Beak Consultants Limited, Brampton, Ontario.	433
BP13	**Tillage and Event Based Soil and Water Loss: Scale Linkages;** R.G. Kachanoski, W.T. Dickenson and R. Rudra, University of Guelph, Guelph, Ontario.	438
BP14	**The Impact of Contaminant Exposure on Mutation Rates in Fish;** L.J. Weider, R. Danzmann, M.H. Murdoch and P.D.N. Hebert, Great Lakes Institute, University of Windsor, Windsor, Ontario.	442
BP15	**Geochemical Associations of Cd, Cu, Pb, Zn, Fe and Mn with Size Fractionated Suspended Sediments in the Don River;** L.A. Warren and A.P. Zimmerman, Department of Zoology, University of Toronto, Toronto, Ontario.	446

BP16 **Assessment of the Biologically-Based Low Flow Analysis Technique;** H.S. Belore and T. Cooper, Cumming-Cockburn Limited, Willowdale, Ontario and I. Gray, B.A.R. Environmental, Guelph, Ontario. 449

BP17 **Regional Analysis of Low Flow Characteristics;** H.S. Belore and D.F. Ashfield, Cumming-Cockburn Limited, Willowdale, Ontario. 454

BP18 **Measurement of Chemical Fluxes from Groundwater to Surface Water;** D. Guyonnet, D.R. Lee, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario. 459

BP19 **Carbon, Sulfur and Nitrogen Cycling in Three Unconfined Sand Aquifer Systems in Ontario;** L. Wassenaar, R. Aravena, R. Gillham, J. Barker and P. Fritz, Institute for Groundwater Research, University of Waterloo, Waterloo, Ontario. 460

BP20 **A Study of the Effectiveness of Ontario's Sport fish Consumption Guidelines;** C.M. Cox, A.L. Vaillancourt and A.F. Johnson, Water Resources Branch, Environment Ontario, Toronto, Ontario. 463

BP21 **Mercury and PCB's in Fish Used as a Major Food Source by Northwestern Ontario Native Peoples;** A.F. Johnson, A.L. Vaillancourt and C.M. Cox, Water Resources Branch, Environment Ontario, Toronto, Ontario. 467

BP22 **Sediment Bioassay Development: Addressing the Pros and Cons;** D. Bedard, Great Lakes Institute, University of Windsor, Ontario. 471

VOLUME II

SESSION C: LIQUID & SOLID WASTE RESEARCH

Verbal Presentations **Page**

C2 **The Mobility and Persistence of Selected Organic Solutes in Anaerobic Groundwaters and Possible In-Situ Remediation Measures;** D.W. Acton*, J.F. Barker, M.A. Shaw, F. Beaudet and J.A. Cherry, Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario. 1

C3 **Experiments on the Efficiency of Forced Air Venting to Remove Volatile Organic Liquids From Soil;** W.B. Benson* and G.J. Farquhar, Civil Engineering, University of Waterloo, Waterloo, Ontario. 9

C4 **Compatibility of Leda Clay with Municipal Solid Waste Leachate;** R.M. Quigley*, F. Fernandez and C. Ohikere, Geotechnical Research Centre, The University of Western Ontario, London, Ontario. 25

C5 **Codisposal of Industrial Waste with Municipal Refuse – An Examination of the Effects of a Hazardous Waste;** S. Pirani*, and D.W. Kirk, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario. 48

C6 **Monitoring and Evaluation of Landfill Cover Lysimeters;** K.J. McKague*, Ecologistics Limited, Waterloo, Ontario and J.H. Cuthill, University of Guelph, Guelph, Ontario. 57

C7 **The Effect of Wellbore Dilution on the Results of Tracer Experiments Conducted in Fractured Rocks;** K.S. Novakowski* and J.A. Cherry, Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario. 68

C8 **Landfill Leachate Recirculation: Effects on Leachate Quality, Clay Surface Infiltration and Plant Vigour;** P.M. Cureton*, P.H. Groenevelt and R.A. McBride, Department of Land Resource Science, University of Guelph, Guelph, Ontario. 78

C9 **Degradation of Organic Solvents in Landfill Leachates;** S. Lesage*, National Water Research Institute, Environment Canada, Burlington, Ontario and P. Riemann and R.A. McBride, Department of Land Resource Science, University of Guelph, Guelph, Ontario. 88

C10 **Physiological and Spectral Responses of Sugar Maple *(Acer saccharum Marsh.)* to Municipal Solid Waste Leachate Spray Irrigation;** S.C. Shrive*, R.A. McBride and T.J. Gillespie, Department of Land Resource Science, University of Guelph, Guelph, Ontario. 99

C11 **Trace Heavy Metal Speciation in Four Landfill Leachates and the Retention of Leachate Cadmium by Soil;** K. Bolton* and L.J. Evans, Department of Land Resource Science, University of Guelph, Guelph, Ontario. 123

C13 **Fish Waste Production, Modelling and Measurement in Relation to Fish Growth in Rainbow Trout Culture;** P.S. Chisholm* and J.G. Farrell, School of Engineering, University of Guelph, Guelph, Ontario. 130

C14 **Glassification and Leachability of Hazardous Wastes and Hazardous Waste Residues;** K.B. Harvey*, D.L. Wilkin and R.J. Porth, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba. 134

C15 **Research and Development of Permanent On-site Solutions for Contamination of Groundwater at Waste Disposal and Industrial Sites in Canada – Phase 1 Update;** P. Hannak*, B. Whiffin*, D. Graham and R. Rush, CH2M Hill Engineering, Ltd., Waterloo, Ontario. 135

C16 **Recycling of Textile Dyebath Effluent;** A.E. Wilcock, University of Guelph, Guelph, Ontario. 150

C17 **Assessment of the Current Waste Management Practices on Farm Operations in Perth County, Ontario;** P. Cahill* and M. Haight, School of Urban and Regional Planning, University of Waterloo, Waterloo, Ontario. 160

C18 **Plasma Gasification of Municipal Solid Waste – Environmental Analyses;** A. Tsangaris*, G.W. Carter, Resorption Canada Limited, Gloucester, Ontario. 173

VOLUME II

SESSION C: LIQUID & SOLID WASTE RESEARCH

Poster Presentations

		Page
CP1	**Development of Backfill and Construction Application Guidelines for Ontario;** M. Kelleher and B. Whiffin, CH2M Hill Engineering Ltd, Mississauga, Ontario.	185
CP2	**Integrated Waste Management Planning in Ontario – Program, Process and Perspectives;** S. Clark, B. Alder, H. Mooij; Waste Management Branch, Environment Ontario, Toronto, Ontario.	186
CP3	**Test of a Chemical/ Mechanical Process for the Decontamination of Non-anatomical Biomedical Waste;** P.L. Seyfried, T. Bleier, E. Bauer and J. Lun, Department of Microbiology, University of Toronto, Toronto, Ontario.	188

VOLUME II

SESSION D: ANALYTICAL METHODS RESEARCH

Verbal Presentations **Page**

D2 **Evaluation of Indoxyl-B-D-Glucuronide, A Novel Chromogenic Reagent for the Specific Detection and Enumeration of *Escherichia Coli* in Environmental Samples;** A.N. Ley*, Environment Ontario, Kingston, Ontario and R.J. Bowers and S. Wolfe, Queen's University, Kingston, Ontario. 203

D3 **Synthesis of Sulphur Polycyclic Aromatic Compounds (PAC) of Interest in Environmental Toxicology;** Y.S. Chung* and E. Lee-Ruff, Department of Chemistry, York University, North York, Ontario. 207

D4 **Flow Injection Preconcentration/Direct Sample Insertion for Trace Element Analysis by ICP/AES and ICP/MS;** P. Moss* and E.D. Salin, Department of Chemistry, McGill University, Montreal, Quebec. 209

D5 **Hot Slurry Sample Introduction for ICP/AES;** E.D. Salin*, L. Gervais and L. Usypchuck, Department of Chemistry, McGill University, Montreal, Quebec. 216

D6 **High Pressure Microwave Digestion in a Stream. A High Efficiency Approach;** E.D. Salin*, and F.H. Li, Department of Chemistry, McGill University, Montreal, Quebec. 224

D7 **Solid Sample Introduction with Pellets for ICP/AES and ICP/MS;** L. Blain*, J. Ren and E.D. Salin, Department of Chemistry, McGill University, Montreal, Quebec. 230

D8 **Retractable Composite Absorbents for Environmental Clean-up;** B. Gillies*, E. Forsberg, M. Garces, R. Li, L. Read and E. Stubley, EcoPlastics Ltd., Willowdale, Ontario and O. Meresz, Environment Ontario, Toronto, Ontario. 238

D9 **Characterization of Leachable Metals in Industrial Wastes: A Suggested Decision Protocol;** J.R. Kramer, Department of Geology, McMaster University, Hamilton, Ontario. 246

D10 **Development of ACexpert. 3. Encoding Rules for AC-diagnosis;** M.J. Stillman*, M. Moussa and Z. Gasyna, Department of Chemistry, The University of Western Ontario, London, Ontario. 254

D11 **Recent Advances in the Determination of Hydride-Forming Elements;** I.D. Brindle*, X-e. Le, Chemistry Department, Brock University, St. Catharines, Ontario. 262

D13 **Application of GC-MS-MS for the Ultra-trace Determination of the Chlorinated Dioxins/Furans;** E.J. Reiner*, V.Y. Taguchi, R.E. Clement, D.H. Schellenberg, D.M. McCurvin, Laboratory Services Branch, Environment Ontario, Toronto, Ontario. 273

D14 **Development of GC Capillary Column for Analyses of Most Toxic Isomer of PCDD, PCDF and PAH in Environmental Samples;** K.P. Naikwadi*, B. Ross and F.W. Karasek, Department of Chemistry, University of Waterloo, Waterloo, Ontario. 280

D15 **Solid Phase Systems for Simultaneous Adsorption/Derivatization of Chlorophenols, Chlorophenoxy Acids and Purification of Products;** J.M. Rosenfeld*, Y. Moharir and F. Matthew-Ahland, Department of Pathology, McMaster University, Hamilton, Ontario. 287

D16 **Immunoassays for Quantitation of Picloram in Soil, Urine, Water and Plants;** R.J.A. Deschamps and J.C. Hall*, Department of Environmental Biology, University of Guelph, Guelph, Ontario. 295

D17 **Determination of the Truly Dissolved Concentration of Organic Contaminants by Headspace Analysis;** J. Resendes*, and D. Mackay, Department of Chemical Engineering, University of Toronto, Toronto, Ontario. 305

D18 **Solid Phase Extraction of Triazines and Organophosphorous Compounds from Drinking Water;** W.G. Craig*, J.M. Craig and A.L. Masse, Paracel Laboratories Ltd., Nepean, Ontario and C.D. Hall, Environment Ontario, Toronto, Ontario. 316

VOLUME II

SESSION D: ANALYTICAL METHODS RESEARCH

Poster Presentations Page

DP1 **Robustness of the Student's T Test with Censored Environmental Quality Data;** E. Creese, Creese Environmental Consulting, Waterloo, Ontario. 323

DP2 **Development of Standard Methodology for the Evaluation of Organic Contaminants Leaching from Municipal and Industrial Wastes;** F.W. Karasek and V. Breitung, Department of Chemistry, University of Waterloo, Waterloo, Ontario. 327

DP3 **A Method of Ultra Trace Metal Determination in Acid Precipitation Samples Using High Performance Ion Chromatography and Inductively Coupled Plasma Source Mass Spectrometry;** M.J. Powell, J. Hipfner and D.W. Boomer, Laboratory Services Branch, Environment Ontario, Toronto, Ontario. 331

DP4 **Extraction and Concentration Method for Testing of Landfill Leachates;** J. Brady, A. Horton, T. Harrison, J. Beetham and G. Thomas, ORTECH International, Mississauga, Ontario. 334

DP5 **Solid Phase Extraction of Polyaromatic Hydrocarbons From Drinking Water;** W.G. Craig, J.M. Craig and R.G. Walker, Paracel Laboratories Ltd., Nepean, Ontario and C.D. Hall, Environment Ontario, Toronto, Ontario. 338

DP6 **Adaptation of Water Preconcentration Techniques of Trace Metal Detection;** J.E. Dowdall and B.R. Hollebone, Department of Chemistry, Carleton University, Ottawa, Ontario. 341

DP7 **Adaptation of Water Preconcentration Techniques Developed for PCDD Analyis to Other Target Organic Pollutants;** C.S. Shewchuk, L.J. Brownlee and B.R. Hollebone, Chemistry Department, Carleton University, Ottawa, Ontario. 348

DP8 **Brominated and Mixed Bromo/Chloro Dibenzo-p-Dioxins and Dibenzofurans: Analytical Methods and Toxicities;** D.S. Waddell, B.G. Chittim and J.M. Sparling, Wellington Environmental, Guelph, Ontario. 353

DP9 **Chlorinated and Nonchlorinated Organics in Storage Studies;** W.M. Neaves and B.B. Fong, Enviroclean, London, Ontario. 354

VOLUME II

SESSION E: ENVIRONMENTAL SOCIO-ECONOMICS

Verbal Presentations Page

E2 **Influence of Valuation Disparities on Judicial Choice and Legal Sanctions;** J.L. Knetsch, Economics Department, Simon Fraser University, Burnaby, British Columbia. 357

E3 **Benefits to Beach Users from Water Quality Improvements;** M.H. Fortin, Ecologistics Limited, Waterloo, Ontario. 365

E4 **Valuation of Water Quality Improvements;** A.P. Bruno*, and P. Blyth, Policy and Planning Branch, Environment Ontario, Toronto, Ontario. 375

E5 **Social Impact Assessment in Waste Management Planning – Where Are We and Where Are We Going;** A. Joyner, M.M. Dillon Limited, Willowdale, Ontario. 389

E6 **Awareness and Participation Levels in High-Rise Apartment Building Recycling Programs;** V.W. Maclaren, Department of Geography, University of Toronto, Toronto, Ontario. 394

E7 **Estimating the Economic and Financial Impacts of New Federal Environmental Requirements Facing Local Governments in the United States;** B.R. Snyder, Economic Studies Branch, Office of Policy Analysis, U.S.E.P.A., Washington, D.C., U.S.A. 401

E8 **An Exploration of Macro-economic Impacts in the Environment-Economy Linkage;** C.A. Sonnen, Informetrica Limited, Ottawa, Ontario. 410

E9 **The Cost of Environmental Protection in the U.S. Through the Year 2000;** K.I. Rubin, Apogee Research, Inc., Bethesda, MD, U.S.A. 418

E10 **Is Ontario's Environmental Protection Regulation Going to Make its Industries Uncompetitive?;** E. Cowan, Apogee Research International, Toronto, Ontario. 427

E13 **Study of the Options for Reduction of Energy-Related Greenhouse Gas Emissions;** E.F. Haites, The DPA Group Inc., Toronto, Ontario. 431

E14 **Costs of Alternate Strategies for Reducing NOx and VOCs Emissions from Stationary Industrial Sources;** T. Sanger*, D. Heeney, and P. Victor, VHB Research and Consulting Inc., Toronto, Ontario and R. Reynolds, SENES Consultants Ltd., Richmond Hill, Ontario. 437

E15 **The Development of an Economic Model to Evaluate Costs for Alternate Strategies for the Management of Toxic Heavy Metal Wastes;** B. Fleet*, and J. Kassirer, University of Toronto, and Toxics Recovery Systems International, Rexdale, Ontario. 449

VOLUME I
FEATURE PRESENTATIONS

Air Quality Research
Water Quality Research
Liquid & Solid Waste Research
Analytical Methods Research
Environmental Socio-Economics

A1

DEALING WITH CLIMATE CHANGE: AN AGENDA FOR THE NEXT DECADE

Extended Abstract for a Presentation to the
1989 Technology Transfer Conference

by
H.G. Hengeveld (Environment Canada)

INTRODUCTION

In June, 1988 a large group of policy makers, scientists, economists, legal and other experts from 46 nations met in Toronto to participate in the World Conference on the Changing Atmosphere. At the conclusion of that watershed meeting, the participants declared that "humanity is conducting an unintended, uncontrolled globally pervasive experiment whose ultimate consequences could be second only to a global nuclear war." They were referring to the rapid change in the composition of the Earth's atmosphere due to human release of pollutants.

During the year since the Toronto Conference, a number of major international statements supported by senior level politicians have declared atmospheric change, and particularly climate warming, a major global environmental issue demanding political action now. Most recently, the World Energy Conference, meeting in Montreal in September, placed unprecedented importance to the issue of Climate warming in its deliberation on energy for tomorrow. Why this rather sudden and intense political and private sector interest in problems of the Earth's atmosphere? How real is the threat to the atmosphere? How certain is the background science and can it justify the concern? If so, what are the implications, and how should we respond?

This presentation will briefly review what the background science can and cannot already say about this issue and, based on the many recommendations that have come forth, suggest some major themes and strategies for responding to it.

EVIDENCE FOR CHANGE

Regular measurements of atmospheric concentrations of CO_2 at numerous stations around the world show a global increase of 11% over the past 30 years. When compared with information obtained from air bubbles fossilized within the Antarctic ice cap, it appears that current values are about 20-25% higher than the previous highest values during at least the past 160,000 years. The principal source of additional accumulation of CO_2 into the atmosphere appears to be the release of carbon as carbon dioxide during the combustion of fossil fuels. The destruction of vast tracts of tropical timberland to make way for agricultural development appears to be a significant secondary source.

Other atmospheric constituents important to climate are also changing rapidly. Methane concentrations, monitored since the early 1970's, are increasing at about 1.1% each year and are already more than double those of pre-industrial times. Although increased global populations of cattle and acreage of rice paddies are believed to be primary sources, release of methane during coal and gas extraction processes and biomass burning are estimated to account for about 40% of the increase. Nitrous oxide is also increasing at 0.3%/year, with an estimated 50% contributed by fossil fuel combustion. Surface concentrations of ozone are increasing in urban areas, largely as a by-product of energy use for transportation. Other gases such as chlorofluoro-carbons, although as yet low in concentrations, are in many cases increasing very rapidly.

The above greenhouse gases have several common features. They are all climatically important gases that already have an abundance sufficient to significantly influence the heat radiation balance of the climate system. They are all increasing in concentration due to human activities. Finally, most are increasing in concentration at least partly due to emissions from the extraction and combustion of fossil fuels.

BASIS FOR CONCERN

Greenhouse gases collectively behave as an insulating blanket around the planet. Their effect on the incoming solar heat energy which fuels the earth's climate system is minimal. However, their combined influence on the outgoing heat radiation, emitted from the earth's surface and lower atmosphere towards space to cool off the climate system, is large. By absorbing and returning much of this outgoing radiation, they effectively trap heat within the lower atmosphere. This "greenhouse effect" is naturally occurring and essential to life on earth. Without it, the earth's surface would be more than 30 degrees C colder. Changing the concentrations of greenhouse gases in the atmosphere will in turn affect the effectiveness of this greenhouse effect.

Projections of future CO_2 emissions into the atmosphere clearly suggest at minimum an eventual doubling of atmosphere CO_2 concentrations over pre-industrial levels. However, the timing of such doubling remains uncertain, since long-term future human behaviour with respect to energy consumption is largely unpredictable. Concentrations of other greenhouse gases are also likely to increase significantly in future decades, adding to the climatic effects of rising CO_2 levels. A combined effect on climate equivalent to a doubling of CO_2 appears possible as early as 2030 AD, and highly probable by 2050 AD.

Atmospheric modellers do not as yet agree on the magnitude of the net climatic changes that would result from an enhanced greenhouse effect. Nor do they agree on the regional characteristics of such changes. However, there is a consensus that such changes will be large, significantly amplified towards polar regions in fall, winter and spring seasons and accompanied by a major adjustment in global rainfall patterns. The range of estimates for the average global surface temperature rise for a CO_2 doubling varies from 1 degree C to 5 degrees C and higher. Most model results also suggest a migration of mid-latitude North American storm tracking northward, resulting in a drier mid-continent and a wetter sub-Arctic.

Climate trends of the past decade indicate that a global climate warming is already in progress. Global temperatures have warmed by 0.4 to 0.5 degrees C over the last century. The six warmest years over that time period have occurred in the 1980's. Although this trend is consistent with model predictions of expected response of climate to changes in greenhouse gas concentrations to date, they are also still within the realms of long-term climate variability, and could be explained by combinations of natural causes for change. While some scientists are already preparing to give the credit to the enhanced greenhouse effect, most feel such conclusions are premature.

Numerous studies have attempted to evaluate how the above changes, should they happen, might affect natural global ecosystems and humans. Some of the consequences are potentially positive. Direct effects of higher CO_2 levels on plants, for example, are beneficial for improved growth and drought tolerance. Warmer temperatures will improve growing seasons in cooler climates, while making polar regions more accessible to marine transportation. However there is great cause for concern in other domains. With almost 50% of the world's human population located along the ocean coastlines, the possibility of a 1 metre or more rise in sea levels has very ominous implications, particularly for low-lying countries such as Bangladesh, Egypt, the Maldives and the Netherlands. Redistribution of rainfall will decrease drought stress in some areas and turn others into deserts, dramatically changing the global pattern of food production and distribution. Slow forest response to climate shifts may result in large-scale dieback along the warm margins of current ecosystems. Heat stress, increased disease, poorer water quality and more frequent severe tropical storms could have major implications for human health and life. Of greatest concern is that the change may be too rapid to make adaptation possible, hence a high risk for catastrophic events.

RESPONDING TO THE CHALLENGE

Numerous international gatherings have attempted to address this question in recent year, including the Conference held in Toronto last year. The consensus appears to be that we must simultaneously attempt to further our research to improve the understanding, prepare for those climate changes that may already be inevitable, and move internationally and domestically to "limit, reduce and, as far as possible, prevent" further climate warming. International law becomes a factor in the second action and a key element in the last. Common conclusions in the international discussion suggest that such legal intervention:

- is inevitably necessary and achievable.

- must be fair and equitable. Developing nations must be an integral part of the solution, but industrialized countries must bear the primary technological and financial responsibilities for reducing emissions of atmospheric pollutants. After all, over 50% of global CO_2 emissions presently come from OECD countries, but all nations will suffer the consequences.
- must be coordinated and cooperative.

This presents a real challenge for international law. No longer are we dealing with bilateral transgressions and damages that can be examined on an aggressor/claimant basis, but with an issue where all nations are, more or less both aggressor and claimant. What is now needed is a much broader umbrella framework Convention that can deal with the atmosphere on a global and more holistic basis and that can appeal to all nations in a 'fair and equitable' basis. Canada is now collaborating with Malta and the United Kingdom in drafting proposed elements for a Global Convention on Climate Change for use in discussions at international meetings.

Meanwhile, domestically we also need to put our house in order. While Canada contributes only 2% of the global emissions of CO_2, it is fourth highest internationally in per capita emissions. Hence the need for national action to reduce our emissions, primarily through improving our energy efficiency, and to promote a public awareness of the issues and implications. In many respects, the latter is the most important, since it is the motivator that should simultaneously remove complacency and avoid hysteria. Conferences, meetings, public hearings and factual literature are required to educate and seek the involvement of scientists, policy makers and public alike. Herein lie the foundations for action.

Finally, a few comments on the implication at the regional level. Where do we, as citizens of Ontario, fit in? The answer lies in the maximum 'think globally, act locally'. First, there is the question of understanding the implication of climate change. While studies under the auspices of the Canadian Climate Program have helped to develop a very crude image of what climate change may really mean, more intensive investigations into sensitivities of our daily activities to climate variances are needed. Muncipal authorities in Waterloo, for example, have already begun to do so. We need greater initiatives of that type elsewhere. Second, we must start to take mitigative action to adapt to climate change that already appears inevitable. In some activities we must wait for greater certainty. In others, such as reforestation programs, we can ill afford to delay, for the trees we plant today will live to see a different climate. Third, we need to begin to do our part locally in limiting the greenhouse gas emissions. Not only are we as individuals among the worst polluters in the world, but our energy inefficiency puts us at great economic disadvantage. Finally, we must do our part in promoting awareness, though our schools, through interaction with the public, and through programs such as that recently launched by Ontario Hydro to reduce energy demand. As Canada's ministers agreed in August, "the consequences of inaction are unacceptable".

B1

Lessons learned from 20 years of experimental manipulations at the Experimental Lakes Area

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The Experimental Lakes Area (ELA) is situated in northwestern Ontario about 80 km east of Kenora, Ont. The site consists of a camp facility and about 45 small lakes in an isolated area on which a variety of studies have been performed over the last 20 years. ELA was established in 1968 by an agreement with the province of Ontario, under the Fisheries Research Board of Canada. It is presently operated by the Experimental Limnology Section of Fisheries and Oceans Canada, Central and Arctic Region. Since the first eutrophication studies were begun in 1968, a large number of experimental manipulations have been performed on lakes, streams, wetland and upland areas, and mesocosms of various sizes. A large body of literature describes (over 400 publications) the scientific advances made in these studies. It would be impossible to summarize these results in a short presentation. This presentation will emphasize the lessons learned by the ELA group concerning the design and operation of experimental manipulations of ecosystems for optimizing the quality and quantity of scientific information. Some of the major discoveries made in the ELA studies will be used as examples of these criteria.

Seven categories have been chosen to describe the criteria which range from details within a experiment such as the development of a specific chemical method to broad questions about interpretation of the results for purposes other than the original goal of the manipulation. The seven categories and sub-categories are shown in Table 1.

Scaling of time and space is a common problem in studies whose results are expected to be applied to other systems. The results of eutrophication studies at ELA, for example, were applied to Great Lakes problems. The acidification studies posed the problem of time scaling as the rate of pH change was higher than that expected in areas impacted by acid rain. Foodweb scaling is a less well known challenge. Experiments in small systems which typically contain limited number of species especially at the higher levels must be applied to more complex systems. This can have a significant influence on factors such as bioaccumulation of toxic contaminants.

Variability is a feature of natural systems which can be forced by climatic changes or biological conditions such as the age and size distribution of fish at the start of a experiment. In the recovery from acidification in Lake 223 the chance invasion of a species at the pH at which it had been lost during acidification is an important uncertainty.

Adaptation to a treatment is dependant on the length and intensity of a treatment and can be manifested by either changes in species composition as has been seen for algae in both the eutrophication and acidification studies or by physiological adjustment as evidenced by fish exposure to toxic metals.

Solutions to some of the above challenges can be provided by controls. Three kinds of controls have been used at ELA. Sets of lakes similar to the experimental ones have been chosen and are monitored during the experiment. In the cases of lakes 302 and 226 lakes with two similar basins were split in two with

Table 1. An outline of the categories of criteria to be addressed in the design and operation of experimental manipulations.

- I.Scaling
    - A.Size
    - B.Time
    - C.Foodweb
    - D.Missing features (eg. hypolimnion)
    - E.Other forcing functions
        - 1.Wind (fetch)
        - 2.Rivers
        - 3.Currents
- II.Variability
    - A.Climatic
        - 1.Precipitation
        - 2.Temperature
        - 3.Cloud
        - 4.Wind
    - B.Biological
        - 1.Population dynamics (eg. age structure)
        - 2.Invasion
        - 3.Growth-Food chain
- III.Adaptation
    - A.Length and intensity of treatment
    - B.Species composition
    - C.Physiological
- IV.Controls
    - A.Similar systems
    - B.Split systems
    - C.Pre/post
- V.Reproducibility
    - A.Replicates
    - B.Other scale trials
- VI.Intensity of effort
    - A.Perturbation scheme
    - B.Sampling frequency
    - C.Precision and new methods vs. stability in time
    - D.Closure (mass balance)
    - E.Technological sophistication
- VII.Applicability or utility outside primary goal
    - A.Cost/benefit
    - B.R&D commitment

curtains. Pre and post treatment data is also collected for experimental systems.

Reproducibility of the experimental manipulations has been addressed to some extent by repeating experiments although costs usually mediate against much replication. Tests of various components of the manipulations have been repeated in several different size mesocosms. These generally have been plastic cloth tubes one to ten meters in diameter suspended from ring floats. Many pilot studies for larger manipulations have also been done in these enclosures.

The intensity of effort applied to a manipulation will be dependant on the kind of situations which one is trying to simulate and the kinds of response in the manipulated systems. Little difference was observed in the Lake 227 experiment when the fertilizer addition was changed from once weekly to continuous feed, however high frequency sampling was necessary to explore the diurnal fluctuation in the concentration of carbon dioxide in the surface waters. For less active components or more linear responses monthly sampling has been sufficient. Intensity of effort also affect precision of the data. A very valuable test of analytical and interpretative success has been the use of mass or charge balances in chemical and biological studies. Defects in the balances often open the door to new insights even though maintaining balances often requires many measurements that might not initially seem necessary.

One of the major successes of the ELA project has been the ability to get a lot of scientific mileage out of each experimental manipulation. This often has been the result of collecting data or preserving samples in such a way as to have them useable for future analyses. This has been done through a commitment to research and development in general an a strong desire to understand how all aspects of natural systems works. This has paid off richly in the long term.

Biographical information

Undergraduate studies and Ph.D. (1976) at Columbia University (Lamont-Doherty Geological Observatory) New York. N.Y.

NSERC Post-doctoral fellowship, Fisheries and Oceans Canada, Winnipeg, 1977-78.

Research Scientist Lamont-Doherty Geological Observatory, Columbia University, 1979-80. Radioisotope tracers of metals and carbon in whole lakes.

Research Scientist, Fisheries and Oceans Canada, Freshwater Institute, Winnipeg, 1981- present.

Section Leader, Experimental Limnology (incl. Experimental Lakes Area) 1987-present.

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Section Leader, Experimental Limnology (incl. Experimental Lakes Area) 1987-present.

C1

DIFFUSION PROFILES IN BARRIER CLAYS; LABORATORY AND FIELD EXPERIENCE

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EXTENDED ABSTRACT

Most modern landfill sites are constructed with a relatively impervious barrier system that is designed to limit the loss of pollutants. The barrier itself may consist of a clay liner only, a flexible membrane in contact with a clay liner or a complex multi-liner system. Leachate drainage layers are normally present on top of each liner system so that large hydraulic head drops do not occur across the liners. With required hydraulic conductivity values as low as 10^{-8} cm/s and very small advective velocities, diffusion becomes the major process for pollutant migration at many sites.

This talk starts with a brief description of the process of chemical diffusion. This is followed by presentation of several diffusion profiles obtained:

(a) in the laboratory at diffusion times of ~ 2 weeks;

(b) in the field at three landfill liner exhumations representing diffusion times from 2 to 10 years;

(c) in the field at the Confederation Road site at times extending from 6 to 18 years;

(d) in the field at a Leda clay site where t = 10,000 years.

Emphasis will be placed on diffusion of species common in leachates which derive from municipal solid waste and comparisons will be made between the diffusion coefficients measured at widely differing diffusion times.

The Chemical Process

Diffusion is the process whereby dissolved chemicals present at "high" concentration migrate towards areas where they are present in lower concentration. The process, while simple in concept, is very complex in reality since a concentration gradient generates osmotic flow, electroosmotic flow and often hydraulic flow, all coupled with the diffusion part of the migration. In dilute "free" solution at $t = 8^{\circ}C$, the diffusion coefficient, D_o, typically varies from ~ 5×10^{-6} cm^2/s for a divalent cation to ~ 15×10^{-6} cm^2/s for a monovalent species such as K^+ or $C\ell^-$.

In a soil water system, increased flow path tortuosity, liquid viscosity, etc. greatly slow the rate of migration and the diffusion coefficient, D_e, for conservative $C\ell^-$ might decrease to a value of ~ 6.5×10^{-6} cm^2/s. If adsorption affects the behaviour of a species (such as K^+ or the heavy metals), D_e drops to very low values as the effect of the distribution coefficient kicks in.

Short Term Laboratory Profiles (Two Weeks)

A large variety of techniques are available for laboratory estimation of diffusion coefficients including constant flux tests (Fick's 1st Law) and transient diffusion tests (Fick's 2nd Law). The latter tests, using actual leachate above an actual test soil, are the most practical method for measuring diffusion coefficients. Recently, Barone et al (1989) showed quite clearly that certain artificial salt solutions may yield diffusion coefficients for $C\ell^-$ that are significantly less than those obtained using real leachate.

Short Term Field Profiles (3 to 10 Years)

Chemical profiles for field diffusion will be presented for two clay liner exhumations at Metro's Keele Valley landfill at t = 2, 3 and 4 years. The chemical profiles for salinity, pH, Na^+, K^+, Ca^{++}, Mg^{++}, $C\ell^-$ and $SO_4^=$ will be presented along with estimated D_e values. A similar set of profiles will be presented for the Glenridge landfill at t = 10 years.

The excavation techniques employed to expose the liner had a marked effect on the profiles, especially the part that extends through the overlying granular drainage layers. An exhumation procedure which leaves the drainage sand in place is recommended.

Chemical profiles have been obtained at the Confederation Road landfill in four separate studies at t = 6, 12, 16 and 18 years. In addition to the above noted species, profiles will be presented for oxygen-eighteen, tritium, dissolved organic carbon and heavy metals.

Long Term Field Profiles (t ≈ 10,000 Years)

Porewater salinity profiles suggesting upward diffusion of salt from Leda clay at Hawkesbury, Ontario will be presented. Smooth curves show the salinity to decrease from ~ 15 g/L at 20 m depth to zero at surface. Extensive geotechnical evidence at the site supports the presence of uniform salinity throughout the clay deposit just prior to erosion of overlying sands about 10,000 ybp. In the absence of groundwater advection, diffusion remains the only removal mechanism and a $D_e = 2 \times 10^{-6}$ cm^2/s may be calculated for paired $NaC\ell$ migration producing "leaching" depths of ~ 20 m.

Studies of long term diffusion by others will be presented if time allows.

Conclusions

Short term landfill profiles and very short term laboratory profiles yield very similar diffusion coefficients provided the laboratory test systems use real MSW leachate. For example, a back-calculated $D_e = 6.5 \times 10^{-6}$ cm^2/s for chloride is reproducible at three landfill sites and in laboratory tests where the moisture contents, background salinities and mineralogy are similar. Conclusions pertaining to the mobility of other species will be presented.

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APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY TO THE ANALYSIS OF MARINE REFERENCE MATERIALS

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Inductively coupled plasma mass spectrometry (ICP-MS) is a relatively new technique for elemental and isotopic analysis which combines the power of the inductively coupled argon plasma as an atomization and ionization source with the sensitivity and selectivity of quadrupole mass spectrometry. The addition of ICP-MS to our existing array of techniques for inorganic trace analysis in 1984 has made a considerable impact on the National Research Council of Canada Marine Analytical Chemistry Standards Program, a program devoted to the development of methods for the determination of trace elements in marine samples, and the production of a family of marine reference materials including both fresh and saline natural waters, marine sediments, and biological tissues. In some cases, the effect has been the replacement of a formerly used method by virtue of the superior performance of ICP-MS. For example, ICP-MS has largely supplanted inductively coupled plasma atomic emission spectrometry (ICP-AES) for the determination of trace elements in natural water reference materials because of its much superior detection power. The capability of ICP-MS for isotope ratio determinations has also been heavily exploited in our laboratory in the performance of multielement isotope dilution analyses, an important component of any reference materials program. The major advantages of ICP-MS over the formerly used method, spark source mass spectrometry (SSMS) are greatly reduced sample preparation and analysis time, and improved precision. In other cases, ICP-MS has complemented other techniques in enabling the certification of additional elements for which there were previously an insufficient number of independent methods of adequate sensitivity. Another complementary effect has been the use of ICP-MS as a very sensitive and selective detection technique for high performance liquid chromatography (HPLC) to address questions of chemical speciation for selected elements such as arsenic and tin. In this paper, the versatility of ICP-MS in marine analytical chemistry is illustrated with three applications carried out in the past year: the determination of 11 trace elements in the coastal seawater reference material CASS-2 after separation by two preconcentration techniques, the multielement analysis of lobster hepatopancreas tissue LUTS-1, and the quantitation of tributyltin and dibutyltin in the harbour sediment reference material PACS-1 by HPLC-ICP-MS.

EXPERIMENTAL

Instrumentation A Perkin-Elmer SCIEX ELAN 500 inductively coupled plasma mass spectrometer was used for all of the work; the instrument has been fitted with an "organics kit", which includes a thermostatted nebulizer spray chamber. The HPLC system used for the tin speciation work consisted of two dual-piston reciprocating pumps (Waters Model 6000) a gradient controller (Waters Model 680), a valve injector (Rheodyne Model 7125) with either a 100 µL or 200 µL loop, and a 10 µm strong cation exchange column (Whatman SCX, 250 mm x 4.6 mm). A second valve, installed immediately after the column, allowed passage of the column effluent either to waste or to the nebulizer of the ICP mass spectrometer via a 0.5 m length of 0.25 mm I.D. Teflon tubing.

Seawater Analysis All sample preparations were performed in a laboratory equipped with laminar air-flow benches and fume cupboards providing a class 10 working environment. Trace elements were separated from 900 mL seawater samples by two procedures. The use of a method involving preconcentration by adsorption on silica-immobilized 8-hydroxy-quinoline (I-8-HOQ) in combination with ICP-MS has been described in detail in three previous publications [1-3]. For 900 mL samples, it yields a concentration factor of 90. A second preconcentration method, involving reductive coprecipitation of trace elements with iron and palladium, reported by Nakashima et al. [4], was found to be suitable for use with ICP-MS with only a slight modification to eliminate the use of hydrochloric acid; this procedure affords a nominal concentration factor of 60. Chromium, nickel, copper, zinc, molybdenum, cadmium, lead, and uranium were determined in the coastal seawater CASS-2 by isotope dilution ICP-MS, while cobalt, manganese, and arsenic were determined by the method of standard additions.

Analysis of Lobster Hepatopancreas LUTS-1. The non-defatted lobster hepatopancreas reference material LUTS-1 is supplied as a stabilized suspension containing 85% water. 1.5 g subsamples of this material were dissolved by sequential microwave digestions with nitric acid and hydrogen peroxide performed with a commercially available microwave oven designed for laboratory applications. Nickel, copper, zinc, strontium, cadmium, mercury and lead were determined by isotope dilution ICP-MS; the methodology has been previously described in detail [5,6]. The monoisotopic elements manganese and cobalt were determined by the method of standard additions.

Determination of Butyltin Species in the Harbour Sediment PACS-1 by HPLC-ICP-MS. A mixture of 4 mL methanol and 8 mL hydrochloric acid was added to a 4 g subsample of dry sediment in a 50 mL borosilicate glass centrifuge tube. The mixture was agitated in an ultrasonic bath for 1 h., after which 4 mL of a mixture of hexane and isobutyl acetate (80:20 v:v) were added. A known volume (usually 0.4 mL) of the hexane/isobutyl acetate layer was drawn off the mixture and evaporated to dryness under a stream of nitrogen. The dry residue was extracted with a few mL of a 0.18 M solution of ammonium citrate in a methanol/water mixture (60:40 v:v); this extract was then diluted to 25 mL with the same solution.

The extraction procedure described above is suitable for the extraction of tributyltin (TBT) and dibutyltin (DBT), but not monobutyltin (MBT). The former two species were easily separated by cation exchange chromatography with a mobile phase of 0.18 M ammonium citrate in methanol/water (60:40 v:v) at pH 6. The concentrations of TBT and DBT in PACS-1 were determined by the method of standard additions using peak height data.

RESULTS

Analysis of the Coastal Seawater Reference Material CASS-2. Results obtained during the recent certification analyses of the coastal seawater reference material CASS-2, presented in Table 1, illustrate the current performance of ICP-MS for seawater analysis. Eight elements (Cr, Ni, Cu, Zn, Mo, Cd, Pb, and U) were determined by isotope dilution ICP-MS while an additional three monoisotopic elements (Co, Mn, and As) were determined by standard additions. Although either of the separation/concentration methods requires several hours, the ICP-MS analysis time for each concentrate is well under 10 minutes. A concentration factor of 50-100 is more than adequate for the determination of most of the trace elements of interest at levels as low as 10-20 ngL^{-1}. In most cases the detection limit is controlled by the procedural blank rather than instrumental sensitivity.

Table 1. Analysis of Coastal Seawater CASS-2. Results in μgL^{-1}

	I-8-HOQ Adsorption	Reductive Coprecipitation	Certified Value
Cr	0.108 ± 0.005	0.129 ± 0.003	0.121 ± 0.016
Ni	0.295 ± 0.010	0.328 ± 0.007	0.298 ± 0.036
Cu	0.669 ± 0.014	0.66 ± 0.04	0.675 ± 0.039
Zn	1.96 ± 0.05	1.89 ± 0.16	1.97 ± 0.12
Mo	-	9.19 ± 0.08	9.01 ± 0.28
Cd	0.021 ± 0.001	0.016 ± 0.001	0.019 ± 0.004
Pb	0.030 ± 0.003	-	0.019 ± 0.006
U	2.78 ± 0.02	2.76 ± 0.02	-
Co	0.039 ± 0.004	0.029 ± 0.002	0.025 ± 0.006
Mn	2.13 ± 0.12	-	1.99 ± 0.15
As	-	1.03 ± 0.06	1.01 ± 0.07

Analysis of the Lobster Hepatopancreas Reference Material LUTS-1. Isotope dilution ICP-MS results obtained for seven elements (Ni, Cu, Zn, Sr, Cd, Hg, and Pb) in LUTS-1, plus standard additions data for Mn and Co, are presented in Table 2. It is noteworthy that the mercury determinations were achieved simultaneously with those for the other elements; although the complete retention of mercury during the digestion procedure has not been demonstrated, it appears that, if partial loss occurs, it must occur after equilibration of the ^{201}Hg isotopic spike has been achieved. Immunity to partial loss of the analyte after isotopic equilibration has been attained is a particularly significant advantage of isotope dilution methodology in the case of mercury.

Table 2. Analysis of Lobster Hepatopancreas LUTS-1. Results in μg/g.

	Found	Certified Value
Ni	0.235 ± 0.011	0.200 ± 0.034
Cu	15.9 ± 0.2	15.9 ± 1.2
Zn	12.4 ± 0.2	12.4 ± 0.8
Sr	2.24 ± 0.04	2.46 ± 0.28
Cd	2.18 ± 0.04	2.12 ± 0.15
Hg	0.017 ± 0.002	0.0167 ± 0.0022
Pb	0.010 ± 0.001	0.010 ± 0.002
Mn	1.20 ± 0.04	1.20 ± 0.13
Co	0.065 ± 0.008	0.051 ± 0.008

Determination of Tributyltin and Dibutyltin in the Harbour Sediment PACS-1. Results for TBT and DBT in PACS-1 obtained by HPLC-ICP-MS are compared in Table 3 with data obtained by gas chromatography with flame photometric detection and by ionspray MS/MS, and with the certified values. The certified values were obtained from a database which includes all the results obtained by the three methodologies developed in this laboratory plus results from five external laboratories which collaborated in the certification process, using their own methods. The TBT and DBT values obtained by HPLC-ICP-MS are in excellent agreement with the certified values. Detection limits for TBT and DBT in sediment samples by this method, estimated using mean sensitivity values from several sets of standard additions data, were 5 ng Sn/g and 12 ng Sn/g, respectively.

Table 3. Determination of Dibutyltin and Tributyltin in the Harbour Sediment PACS-1.

Technique	DBT	TBT
	µg Sn/g dry weight	
HPLC-ICP-MS	1.19 ± 0.14	1.18 ± 0.15
GC-FPD	1.07 ± 0.31	1.14 ± 0.27
ISMS/MS	-	1.29 ± 0.07
Certified Value	1.16 ± 0.18	1.27 ± 0.22

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E1

TOWARDS A BETTER INTEGRATION OF ENVIRONMENTAL, ECONOMIC AND OTHER GOVERNMENTAL POLICIES

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The experience gained by OECD Member countries during recent years has shown that anticipate and prevent strategies have a better chance of being implemented through a closer integration of environmental policy with economic policy and policies in specific sectors such as agriculture, energy, industry, development aid, health, land use, tourism and transportation. Efforts have already been made towards this direction. However, further progress will only be made if four main needs are fully addressed:

-- the need for a better internalisation of social costs;

-- the need to remove contradictions between environmental and economic and other sectoral policies;

-- the need to develop and use more appropriate tools for better integrating environmental considerations into economic decision-making;

-- the need to establish more appropriate legal administrative and institutional arrangements.

The need for a better internalisation of social costs

The Polluter-Pays Principle which has been adopted by the OECD, is a principle of partial internalisation of the costs of pollution. A fuller internalisation of social costs would imply an extension of its scope to cover non-point sources of pollution and an investigation into how compensation and insurance schemes can contribute to a more effective implementation of the principle. A better internalisation of social costs might also be encouraged by a more effective use of economic instruments.

The need to remove contradictions between environmental and economic sectoral policies

Another potentially influential strategy based on market signals consists of correcting governmental interventions which have proved to introduce distorsions into the valuation of environmental resources. The most obvious examples of such interventions are: subsidies, price controls, quality control and regulation of activity. To ensure a better integration of environmental considerations into the various sectoral governmental policies, it is essential, as a first step, to identify those interventions by governments which prove to be detrimental to the environment and, secondly, to develop policy reforms in order to eliminate them. Examples will be given of the need to remove contradictions between environmental and economic sectoral policies on the basis of the work carried out by the OECD Environment Directorate in major economic sectors such as agriculture, transport and water resource management.

The need to develop and use more appropriate tools for better integrating environmental considerations into economic decision-making

The integration of environmental considerations into economic decision-making would be facilitated if environmental values were incorporated systematically into standard cost benefit analysis. There is a growing body of benefit studies in terms of physical impacts and money terms which have been developed recently in the OECD Member countries. However, the results of such studies are now frequently used in actual decision-making.

At the macro level there is also a need to refocus attention on the way economic success is recorded and measured, especially in the national income accounts. The paper will review briefly efforts under way in OECD countries to integrate environmental and economic accounts.

The need to establish more appropriate legal administrative and institutional arrangements

Finally, using market signals alone to integrate environmental considerations into economic and sectoral policies is not enough. If integration is to occur, a number of conditions need to be met. First, explicit political credibility for integration should be given through political commitment; second, organisational structures and institutional arrangements must be considered; third, processes and mechanisms which facilitate discussion and interaction among participants must be created; and fourth, mechanisms for further strengthening public participation should also be promoted.

A12

Recent Developments in Applied Dispersion Modeling

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1. Introduction

Air pollutants disperse in the planetary boundary layer (PBL), the turbulent air layer next to the earth's surface that is controlled by the surface heat and momentum fluxes. Much progress has occurred in our understanding of the PBL's turbulence structure over the past 20 years (Wyngaard, 1988), and this along with laboratory experiments (e.g., Willis and Deardorff, 1978) has advanced our understanding of diffusion and has led to improved dispersion models.

This review focuses on dispersion model developments for point-source releases of nonreactive pollutants, concentration averaging times of about an hour, and downwind distances of ~ 20 km or less. The most significant model improvements have occurred for dispersion in the convective boundary layer (CBL) which is when maximum ground-level concentrations (GLCs) usually occur for tall stacks in flat terrain. Improved models have also been developed for vertical dispersion in the stable boundary layer (SBL) and several other problems—dispersion in complex terrain, shoreline fumigation, and dense gas dispersion. This abstract highlights some of these advances; their implications for regulatory practice will be discussed in the presentation.

2. Dispersion in the Convective Boundary Layer

CBL Properties. The CBL extends from the ground to the base of an elevated inversion and is characterized by strong vertical mixing driven by an upward heat flux. The convective eddies—updrafts and downdrafts—are large with dimensions that are proportional to the CBL depth, h, and velocities that are proportional to the convective velocity scale, w_*; $w_* = (g\overline{w\theta_o}h/\Theta_o)^{1/3}$, where g is the gravitational acceleration, $\overline{w\theta_o}$ is the surface heat flux, and Θ_o is the mean potential temperature. At midday over land, typical values of h and w_* are 1 to 2 km and 2 m/s, respectively.

Mechanical turbulence due to flow over the rough surface scales with the surface friction velocity, u_*, and is confined mostly to shallow heights (z), $z < -L$, where L is the Monin-Obukhov length; $|L|$ is typically 10 to 100 m. The stability parameter characterizing the relative importance of convective and mechanical turbulence throughout the CBL is $-h/L$, with useful alternatives being w_*/u_* or w_*/U, where U is the mean wind speed in the CBL (Weil, 1988). These replace the Pasquill stability class during daytime.

Within the "mixed layer" ($0.1h \lesssim z \lesssim h$), the mean wind and the crosswind (σ_v) and vertical (σ_w) turbulence components vary little with z; in dispersion applications, the turbulence is usually assumed to be uniform with $\sigma_v, \sigma_w \sim 0.6w_*$. For dispersion, an important characteristic is the non-Gaussian probability distribution of vertical velocity, w; the distribution is positively skewed. This is consistent with the observation that downdrafts occupy a greater fraction (0.6) of the horizontal surface area than do updrafts (see Weil, 1988).

Dispersion of Passive Plumes. The main features of nonbuoyant plume dispersion in the CBL were first shown through laboratory experiments (Willis and Deardorff, 1976, 1978) and numerical simulations (Lamb, 1982) and later confirmed by field observations (Eberhard et al., 1988). For a near surface source, the average plume centerline, as defined by the locus of maximum concentration, ascended after a short downwind distance whereas the centerline from an elevated source descended until it reached the ground. The elevated plume descent was explained by the greater areal coverage by downdrafts, and thus, the higher probability of material being released into them; the surface plume ascent resulted from the "sweep out" of material into convergence zones near the surface before material initially carried aloft recirculated down (Lamb, 1982). These behaviors differed significantly from the conventional Gaussian plume model.

These experiments and simulations stimulated the development of a new dispersion model—the p.d.f. approach—which is based on the probability density function (p.d.f., p_w) of w (Misra, 1982; Venkatram, 1983; Weil and Furth, 1981); the model applies to elevated sources with heights $z_s > 0.1h$. "Particles" from a source are assumed to be emitted into convective elements—updrafts and downdrafts—having a horizontal speed U and a vertical velocity (w) that is random and specified by p_w. A key assumption is that the Lagrangian time scale, which measures the turbulence "memory," is very large; this means that a particle's velocity at any downwind distance, x, is uniquely determined by its initial velocity. The crosswind-integrated concentration (CWIC), C^y, is found from the p.d.f. of particle height, z_c, which in turn is found from p_w. The models give C^y predictions at the surface that are in qualitative and, in some cases, good quantitative agreement with the laboratory and numerical simulations (also see Weil, 1988). The GLC, C, is found from C^y by assuming a Gaussian crosswind distribution, i.e., $C = C^y/\sqrt{2\pi}\sigma_y$.

For elevated sources ($z_s > 0.1h$), statistical theory predicts the vertical dispersion parameter, σ_z, to be $\sigma_z/h = 0.6X$ where the dimensionless distance $X = w_* x/Uh$. This theory is approximately correct because of the near uniformity of σ_w in the mixed layer (Weil, 1988). For $X > 0.7$, σ_z/h approaches a constant ($\sim$ 0.3 to 0.4) due to plume trapping by the elevated inversion. Plumes from surface sources spread at a faster rate, $\sigma_z/h \propto X^{3/2}$, due to the variation of σ_w with z near the surface. The above results are supported by observations from oil fog and radar chaff plumes (Briggs et al., 1986).

Dispersion of Buoyant Plumes. The laboratory experiments by Willis and Deardorff (1983) showed that the dimensionless buoyancy flux F_* is the most important measure of plume buoyancy effects far from a stack; $F_* = F/Uw_*^2h$ where F is the stack buoyancy flux. These experiments and our better knowledge of CBL turbulence have been used to develop or improve three types of applied models: 1) the Gaussian plume, 2) the p.d.f. approach with plume rise included, and 3) the impingement model.

Weil and Brower (1984) and Berkowicz et al. (1986) improved the Gaussian model by including dispersion parameters and stability estimation methods using the new CBL information. Weil and Brower adopted Briggs dispersion curves, which were for elevated sources and were consistent with the short-range limit of statistical theory; the curves were selected using U/w_* as the stability parameter. Berkowicz et al. developed expressions for σ_y and σ_z explicitly in terms of w_*, u_*, h, z_s, and x. These models included Briggs' (1984) formulas for final plume rise in convective conditions and for plume penetration of the elevated inversion.

Weil and Brower evaluated their model with SO_2 GLCs downwind of Maryland power plants, and showed that it performed much better than the EPA CRSTER model, which is based on the Pasquill-Gifford-Turner stability classification method. The data were obtained during daytime convective periods. Another evaluation by Tikvart and Cox (1984) showed that the Weil/Brower model overestimated the maximum SO_2 GLCs around the Clifty Creek power plant by factors of 2 to 3. The highest concentrations were predicted for light winds ($U \lesssim 2$ m/s) and low h ($\lesssim 700$ m), i.e., for $F_* > 0.1$ and with the plume trapped beneath the elevated inversion. The model was recently modified for this problem and was found to perform much better (Weil and Corio, 1988).

The p.d.f. model for buoyant plumes (Weil et al., 1986) is divided into "low" and "high" buoyancy flux regimes—$F_* < 0.1$ and $F_* > 0.1$— respectively, based on the laboratory experiments. For $F_* < 0.1$, Weil et al. superpose the vertical displacements due to source buoyancy and convection to find the "instantaneous" plume centerline height: $z_c = z_s + 1.6(F^{1/3}/U)x^{2/3} + wx/U$, where the second term on the right-hand-side is the familiar "two-thirds law" for plume rise (Briggs, 1984). The CWIC in the instantaneous plume (C^y_b) is assumed to have a Gaussian distribution about z_c, and the ensemble-mean C^y is found by averaging C^y_b over all possible values of z_c. This results in simple expressions for C^y and the GLC.

For $F_* > 0.1$, the plume is assumed to rise to the top of the CBL, where it "lofts" or lingers until individual cross-sections are mixed to the surface by downdrafts. The key assumptions are that: 1) a plume cross-section remains within the same downdraft until it is uniformly mixed in the vertical ($C^y = Q/Uh$ where Q is the source strength), and 2) plume segments become uniformly mixed only when a downdraft has sufficient kinetic energy ($\propto w^2$) to overcome the potential energy difference between the plume and the environment ($\propto gh$). The ensemble-averaged C^y at the surface is Q/Uh times the probability, P_m, that uniform mixing has occurred; P_m is found from p_w, the energy criterion for uniform mixing, and other considerations.

Evaluation of the p.d.f. model with SF_6 GLCs downwind of the Kincaid power plant showed fair to good agreement. The geometric mean (GM) and geometric standard deviation (GSD) of C_{pred}/C_{obs} were 1.1 and 2.1, respectively, where C_{pred} and C_{obs} are the predicted and observed GLCs. In addition, 68% of the predictions were within a factor of 2 of the observations. In contrast, the CRSTER model exhibited greater scatter (GSD = 4.6) and fewer predictions within a factor of 2 of C_{obs} (33%).

Venkatram's (1980) impingement model is similar to the p.d.f. approach in that plume rise is considered relative to updrafts and downdrafts. The GLC is found from an assumed p.d.f. of the "impingement" distance, which is where plume segments in downdrafts first touch the ground. Evaluation of the model around tall stacks showed good performance; in principle, it is probably most applicable for $F_* < 0.1$.

3. Dispersion in the Stable Boundary Layer

SBL Properties. Turbulence in the SBL is generated by wind shear, i.e., by flow over the rough surface, and is destroyed by stable buoyancy forces. It is much weaker than CBL turbulence and is characterized by small velocity fluctuations and length scales as well as strong height variations. The SBL height typically ranges from ~ 10 m to a few hundred meters. Observations and calculations show that the turbulence velocity scale is u_* which is typically 0.1 m/s to 0.3 m/s in stable conditions. The turbulent eddies are proportional to z near the surface and attain a limiting value of σ_w/N far from the surface, where N is the Brunt-Vaissala frequency, $[(g/\Theta)(\partial\Theta/\partial z)]^{1/2}$, and Θ is the potential temperature at z; σ_w/N is typically 10 m.

Dispersion. For vertical dispersion of passive material from surface sources, van Ulden (1978) developed a simple model based on eddy-diffusion (K) theory and obtained good agreement between predictions and observations of the surface C^y values. Venkatram (1988a) combined statistical theory with other assumptions to obtain simple expressions for σ_z and C^y. For short travel times t, he found $\sigma_z \propto u_* t$ and $C^y \propto Q/u_* x$; for long times, he obtained $\sigma_z \propto L^{2/3}x^{1/3}$ and $C^y \propto Q/u_* L^{1/3}x^{2/3}$. Venkatram also showed good correlation between these C^y expressions and observations. These models are based on a realistic wind profile, $u(z)$, where $u(0) = 0$; thus, they avoid the problem in regulatory models of choosing some representative wind speed for a surface release.

For elevated sources, Venkatram et al. (1984) used statistical theory to predict the vertical dispersion which behaved as $\sigma_z \propto t^{1/2}$ over most of the observed distance range, $x < 1$ km. The $t^{1/2}$ dependence resulted from the small turbulence length scale (σ_w/N) and time scale ($\propto N^{-1}$) in the upper part of the SBL; the theory predicts that σ_z varies as $t^{1/2}$ when $Nt > 1$. Another model by Pearson et al. (1983) predicts that σ_z approaches a constant proportional to σ_w/N for $Nt > 1$. Both types of behavior can be deduced from the measurements reported by Venkatram et al. (1984).

For elevated buoyant plumes, high GLCs can occur in a weakly stable environment coupled with high winds. Venkatram and Paine (1985) addressed this problem with a model akin to the Gaussian plume, but they took into account the variation of σ_w with z. This was done by computing σ_z separately above and below the plume centerline. Their model evaluation with GLC data around tall stacks demonstrated good performance and much better than that attained with the CRSTER model.

4. Other Problems

Dispersion in Complex Terrain. Two major complex terrain problems have been investigated in recent years: 1) dispersion or "impingement" of stack plumes on the windward side of hills, and 2) dispersion within narrow valleys. This discussion focuses on the first which has been significantly advanced due to a much better understanding of the flow field about hills. Such understanding is due largely to laboratory experiments of flow about three-dimensional hills in a stratified towing tank (Hunt and Snyder, 1980). The main result is that in strongly stable conditions fluid below a "dividing streamline height," h_c, passes around the hill in nearly horizontal planes, whereas above h_c, fluid passes both over and around the hill. The inability of fluid below h_c to surmount the hill is due to its insufficient kinetic energy, i.e., to overcome the potential energy barrier determined by h_t and the stratification. The experiments show that $h_c = h_t(1 - Fr)$ where h_t is the hill height and Fr is the hill Froude number, $Fr = U/h_tN$. This is valid for $Fr \leq 1$; for $Fr > 1$, the fluid is able to flow over the hill from essentially any initial upstream height.

In neutral flow ($Fr \rightarrow \infty$) over a hill, potential flow can be used to predict the centerline path about the hill and the GLCs for a Gaussian plume embedded in it (Hunt et al., 1979); this model accounts for the plume deformation by the flow field and the speed-up over the hill. Egan (1975) used this approach earlier to determine terrain adjustments to the "effective stack height," h_e, and suggested a half-height correction, $h_e - h_t/2$.

For $Fr < 1$, the plume trajectory and GLCs depend on h_s/h_c. For $h_s < h_c$, the plume is in the horizontally flowing layer and can impinge on the hill with maximum GLCs equal to those on the plume centerline (at the same x) in the hill's absence (Hunt et al., 1979; Synder and Hunt, 1984). For $h_s > h_c$, the potential flow model can be used above h_c with the flow about a "cut-off" hill, $h_t - h_c$. The dividing streamline concept is used in RTDM (developed by ERT), a model now used as a screening approach by EPA. The model predicts lower GLCs than the VALLEY model and has been found to agree better with observations. Another improved model using the h_c concept and others is CTDM which is under development for EPA (see Venkatram, 1988b).

Shoreline Fumigation. This problem exists near large lakes or coastlines when a stable onshore flow passes over a heated land surface. A growing thermal internal boundary layer (TIBL) develops from the leading edge of the land surface and plume fumigation occurs when this unstable layer intercepts the elevated, stabilized plume. Misra (1980) developed a model which assumes the plume to be a continuous source of pollutants along the TIBL–plume interface. The pollutant flux through the TIBL top is based both on the TIBL growth rate and the dispersion of the stabilized plume prior to fumigation. With this flux specified, the concentration field within the TIBL is found by superposing the concentrations due to all the elemental sources along the TIBL top; a uniform vertical distribution is assumed in the TIBL, implying "instantaneous" vertical mixing. Crosswind dispersion within the TIBL is determined by its local height, $h(x)$, w_*, U, and x which are the relevant parameters based on the CBL discussion.

Misra and Onlock (1982) found good agreement between model-predicted GLCs and SO_2 measurements downwind of the Nanticoke Generating Station on the Lake Erie shoreline. Further discussion of this and other models as well as predictive methods for the TIBL height are reviewed by Venkatram (1988b).

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Environment Ontario
B12 Environmental Research - Technology Transfer Conference
Water Quality Session
Toronto, November 21, 1989

International Perspectives on Drinking Water Research

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ABSTRACT

Introduction

Research in the Water Supply area is expanding rapidly: worldwide budgets have more than doubled since the onset of the decade. It is a rather new phenomenon, surprising in a profession generally seen as quite conservative, which is primarily aimed at giving the public a better quality water.

A recent survey was presented at the "International Water Supply Association", Rio-de-Janeiro congress, in September of 1988. It focuses on the understanding of the reasons of this new trend. It also sheds some light on the future of the drinking water quality.

The Reasons for the Growth in Research

The forces which drive the water supply profession to increase its research can be divided into two main categories: the first come from outside the profession and are relatively beyond its control and the second are linked to the specific context and the "strategy" of each water service.

- External forces. A certain number of exogenous forces can be identified. Among them the tightening of quality standards accompanied by an overall increase in consumer demand for water quality is probably the strongest one. The general progress in technology (computer Science, biotechnology membrane separation,....) and the trend toward privatization of services are also important reasons for the increase in R & D.

- Internal Forces. They come from the water service itself and are of course influenced by the latter. The search for productivity, the development of water metering, the need for a closer relationship with the consumers, the drive for quality, the motivation of the staff,... are all powerful drives.

The Influence of Regulations

The new regulations and more particularly the U.S. EPA Safe Drinking Water Act and the European Community Water Quality Standards, are strong incentives in the increase in R & D on treatment technologies. They also triggered a new era of work on analytical techniques, health assessments and toxicity measurement.

It seems unlikely, however, that water quality standard will keep being reinforced beyond the early part of the next decade. The question is thus, will the research drive remain sustained after that? The answer seems to be yes, because of the influence of the other external forces.

Who does what?

Looking at the world at wide:

- Research by the water supply organization themselves whether public or private is increasing rapidly. Often this research is done in a cooperative way.

- The relative importance of national or professional collective research centres, (such as the WRC in England or the KIWA in the Netherlands) established over the past two decades is decreasing.

- University research, particularly strong in the United States is still important but shows no signs of growth either. It has a particular importance, however, since it is the starting point for new research and is centred on basic research which generates true innovation.

- Research activity by consulting engineering firms is a still relatively limited phenomenon but one which is growing, especially in the United States.

- In terms of funding, there is an overall
  - decrease in central (national) government funding;
  - increase in international funding, particularly strong in Europe (e.g. Eureka Program)
  - increase in collective professional funding (AWWARF in the USA, SVW in Belgium, etc.) and above all,
  - increase in direct professional funding.

The Areas of Research

The majority (more than 50%) of the research effort is still on water quality and treatment. Within this category a great deal is spent in pilot experiments and primarily on activated carbon and ozone. Emerging technologies - such as membrane separation - are slowly moving in, pulled by specific market requirements (i.e. in this case, the Florida market). Health effect studies are regaining importance. There is a general increase in the work on the distribution system: hydraulic problems, pipe renovation, mapping,... but also corrosion and changes in water quality in the distribution network. A new area of interest is the improvement of the relationship with the consumers.

The Organization of Research

A number of organizational features are being developed within the water services in order to cope with this rising need for research. It usually starts with an involvement of the general management of the water organization. It includes the development of an analytical structure and the hiring of personnel having a background in chemistry. It also includes, at the world level, a higher involvement of the professional associations such as IWSA and AWWA. The relative importance of research oriented papers in the professional conferences is thus naturally increasing and contributes in turn to the acceleration of change.

Conclusion

This wave of increasing research efforts may impact considerably on the water supply profession and it appears likely that today practices will undergo great changes over the next decade.

In Canada, where water resources seem to be unlimited and regulations of small constraint, the situation may change as well. The motivations, however, may be somewhat different. Through the development of new and proprietary technologies, with the help of a Government determined to be at the fore-front of environmental issues and above all through the organization of a systematic cooperative research between the different partners of the water sector; utilities, government, industries, this country might be a world leader in drinking water supply by the turn of the century.

C12

ABSTRACT

THE SOLID WASTE ISSUE: THE PLASTICS INDUSTRY'S INITIATIVE

Do we have a Solid Waste Dilemma? We certainly do! Are plastic products part of the Solid Waste Issue? They certainly are! Is the Plastics Industry responding to the challenge? They certainly are! The answers to these and other questions are addressed in this paper which will outline the initiatives being taken by the Plastics Industry in Canada within the framework of Global activity.

The Canadian Plastics Industry recognizes that it is part of the Solid Waste Issue and is determined to be a part of the Solid Waste Solution. Industry representatives are working on their own initiatives but as important is the work being done through the industry's association, The Society of the Plastics Industry and its umbrella group The Environment and Plastics Institute of Canada (EPIC). EPIC was formally launched in March, 1988 and has as its mandate:

> TO DEMONSTRATE OUR COMMITMENT TO A CLEAN ENVIRONMENT,
>
> TO ADVANCE OUR INDUSTRY'S DESIRE TO EARN AND MAINTAIN PUBLIC TRUST AND
>
> TO FOSTER EFFECTIVE, RESPONSIBLE SHORT AND LONG TERM SOLUTIONS TO CONCERNS REGARDING PLASTICS WASTE DISPOSAL.

ABSTRACT

THE SOLID WASTE ISSUE: THE PLASTICS INDUSTRY'S INITIATIVES

M.A. HYDE

The industry believes that the answer to the solid waste issue does not lie in a single solution but rather a combination of solutions that have been dubbed the six "R's" - namely REDUCE, REUSE, RECYCLE, RECOVER, RETENTION, and RESEARCH.

A study of each of these "R's" is presented with emphasis on the Research "R" which crosses the boundaries of all of the solutions.

The degradability issue is discussed and the pros and cons of degradability outlined.

The paper concludes as it outlines the magnitude of the task that confronts Canada and in fact the World.

M.A. Hyde
September 26, 1988

D12

AMBIENT PRESSURE IONIZATION METHODS FOR ENVIRONMENTAL ANALYSIS

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Ambient pressure ionization detection methods such as the flame ionization detector (FID), the photoionization detector (PID), the thermionic detector (TID) and the electron capture detector (ECD) have been used extensively after chromatographic separation for the routine analysis of environmental samples. In general these detectors are of simple design consisting of an energy source (a flame, a lamp, a hot surface, or a radioactive foil) and an electrode to collect ions created from the sample through interaction with the energy source. The simplicity of these devices, relative to mass and light spectrometers, have lead to their popularity for use with routine analytical methods.

While such ambient pressure ionization methods are often sensitive with ionization efficiencies greater than 10^{-3} ions/molecule, responses are generally more universal than selective. For example, the flame ionization detector and the photoionization detector respond to most organic compounds while the electron capture detector responds to all electronegative compounds. Selective response can be of paramount importance for the analysis of complex environmental samples where the possibility of matrix interferences is great. Of the ambient pressure ionization detectors, only the TID provides selective responses based on unique ionization properties of nitrogen and phosphorus containing compounds.

Whether ionization is based on chemi-ionization as in the FID, ionization potential as in the PID, electronegativity as in the ECD or surface ionization as in the TID, response selectivity is generated in the ionization step. Response selectivity can be achieved in the collection step as well as the ionization step, producing more selective, yet still sensitive, ambient pressure ionization detection methods for environmental analysis. By taking advantage of differences in gas phase mobilities of response ions, unique and often spectacular selective responses can be achieved.

In this presentation, unique selective responses generated using common detection methods that have been modified to select response ions based gas phase mobilities will be demonstrated for a variety of environmental samples. For example, a photoionization detector coupled with an ion mobility drift tube can be used for the selective response of aromatic compounds.

Also, an electron capture detector coupled with an ion mobility drift tube can be used for the selective detection of chlorinated compounds in the presence of other electronegative compounds. Brominated compounds can be selectively detected in the presence of chlorinated compounds and, in certain cases such as 2,4-dichlorophenoxyacetic acid, compound specific detection can be achieved. In the positive mode (i.e. monitoring positive response ions) tunable selective response of sulfur, nitrogen, and phosphorus containing compounds can be achieved.

With the flame ionization detector, conditions have been found where both unique ionization processes coupled with mobility selection have lead to an ionization method selective for organometallic compounds such as organoleads and organotins. The determination of organoleads in gasoline and of organotins in fish samples are two example applications which will be presented. In addition, conditions have been determined in which this flame ionization detector will respond selectivity to silicon containing compounds. Examples in which organic acids adsorbed onto particulate matter have been derivatized and selectively detected by flame ionization illustrate that derivatization can be used to tag compounds of interests for selective detection as well as to enhance chromatographic behavior.

In all of the applications presented above, the ambient pressure gas phase mobility of ions plays an important role in the selection of the dominant analytical response.

E12

Economic Evaluation of Global Warming Policies

D.N. Dewees

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Sept. 28, 1989

I. Introduction

A frightening set of environmental manifestations during the last two years, from hot dry summers to the growing hole in the ozone, have convinced the general public that environmental concerns may directly affect every one of us. This public concern has generated powerful demands for political action to control global pollutants. Indeed, at least ten bills have been introduced into the U.S. Congress within the last year dealing specifically with global environmental problem. The 1988 Toronto Conference has been followed by the deliberations of a Federal-Provincial Task Force, which has received a report stating that solutions to global warming will be extremely difficult to achieve. (DPA, 1989.)

The struggle over environmental protection during the last several decades has been primarily a struggle over local pollution problems. Large amounts have been spent to date and much greater expenditures may be expected in the future. Yet the difficulties in achieving the present level of environmental quality will seem small compared to the difficulties in controlling global pollutants, if serious controls are to be achieved. This paper will discuss some contributors to global warming, review existing environmental policies, identify proposals for dealing with the global pollutants, and evaluate policies that are likely to be necessary to have a substantial impact on those problems. I will conclude that substantial reductions in global pollutants will require vigorous policies that will in turn have a significant impact on energy consumption, and some effect on trade in energy resources.

II. Pollutants and Controls

A. Carbon Dioxide

The primary harm caused by carbon dioxide (CO_2) is the greenhouse effect leading to global warming. Carbon dioxide concentrations in the atmosphere have increased perhaps twenty-five per cent since the beginning of the industrial revolution, and currently are increasing at a rate of 0.4 per cent per year. (EPA, 1989, p. 15.) Carbon dioxide, like other greenhouse gases, allows short wave length solar radiation including visible light and ultraviolet radiation from the sun to pass through to the earth's surface, but absorbs a long wave length (infrared) radiation from the earth's surface, trapping heat that would otherwise radiate to space. Continued increases in CO_2 and other greenhouse gases may lead to global warming with consequent flooding of seacoast areas, increases in weather variability, and the expansion of some deserts.

Carbon dioxide is a natural constituent of the earth's atmosphere emitted by a number of natural processes and removed by plants and other aspects of the ecosystem. The major man-made source of carbon dioxide is the burning of fossil fuels. Since fossil fuels are composed primarily of carbon and hydrogen, their combustion invariably yields CO_2 and water vapour. The carbon content per unit of heat in the fuel is in the ratio of about 10 to 8 to 6 for coal, oil, and natural gas respectively, reflecting the differing ratios of carbon to hydrogen in those fuels. There is no practicable means for controlling carbon dioxide emissions once carbon combustion has taken place, and little prospect that practicable control technology would emerge in the foreseeable future.

In the case of most other pollutants, it is possible to reduce emissions without reducing the underlying economic activity. Thus particulate emissions from power plants can be reduced by more than 99% while holding electricity generation constant by installing baghouses. Sulphur dioxide emissions from coal-fired power plants or non-ferrous smelters may be reduced by 50% and more without reducing the amount of electricy generated or the amount of metal produced by burning low-sulphur coal, installing scrubbers, or changing the smelting process. In the absence of technologies that reduce the CO_2 emissions per unit of fuel burned, it is necessary to reduce carbon combustion, a much more difficult proposition.

Two recent reports (EPA, 1989; DPA, 1989) review the technological possibilities for reducing total carbon combustion, which fall into three general groups: conserving on the end-use consumption of fossil fuels; reducing the demand for electricity; and switching from fossil fuels to other sources for electricity generation. A vast array of specific technologies might be employed to reduce end-use consumption of fossil fuels and of electricity, including: application of solar energy, high efficiency oil and gas appliances, improved building insulation, improved insulation of hot water systems, cogeneration, shifting travellers from automobile to bus or rail, urban traffic management, improved transportation vehicle efficiency, substitution of heat pumps for other heat sources, and the use of high efficiency electrical appliances of all types (lighting, motors, air-conditioning).

B. Other Greenhouse Gases

Other greenhouse gases include chlorofluorocarbons (CFC's), methane, ozone, and water vapour. Chlorofluorocarbons are important both as greenhouse gases themselves and because they tend to destroy the stratospheric ozone layer which offers protection against solar radiation. CFC's are used as refrigerants and for various purposes. Methane is emitted from a variety of natural biological sources (such as rice production) from mining activities (as a byproduct of coal mining) from decomposition of garbage in solid waste disposal sites, and other sources. Water vapour of course is a byproduct of all fossil fuel combustion.

In the case of chlorofluorocarbons, reductions in consumption are feasible because of the emergence of substitute materials that provide similar performance but without the damaging side effects. The discharge of water vapour from fossil fuel combustion seems unavoidable unless there is sufficient demand for low temperature heat that the exhaust gases can be cooled to the point where the water vapour condenses. While this is actually achieved in high efficiency condensing furnaces for domestic heating, it seems very unlikely for commercial applications. Control of at least some of the methane sources is feasible. The most difficult greenhouse gas control problems thus appear to be associated with CO_2 emission reductions.

C. Stocks Versus Flows

To understand the magnitude of the demands for controlling global pollutants one must understand the distinction between stock and flow pollutants. A flow pollutant is one which has a very short residence time in the environment, because it degrades and becomes harmless, or because it is removed by natural mechanisms. If the residence time is short, then a reduction in emissions today means a reduction in ambient concentrations tomorrow. An example would be the discharge of large particulate matter to the atmosphere. Because large particulates settle out rapidly, reduced emissions are quickly translated into improved environmental quality.

In contrast, a stock pollutant is one with a long residence time in the environment. The long residence time results both from the chemical persistence of the substance and from removal mechanisms that operate slowly relative to the discharge rate. The stock of the pollutant in the environment at any given time is large relative to the daily emission rate. It follows that a reduction in emissions today has a negligible effect on the ambient concentration tomorrow. Indeed, even a complete cessation of discharge may not substantially reduce ambient concentrations for decades. The global pollutants discussed here are to a large extent stock pollutants. In the case of carbon dioxide, decades would be required to significantly reduce ambient concentrations as a result of even a sharp reduction in current discharges. In the case of CFC's, it is estimated that these have a residence time of 50 to 100 years in the atmosphere, so that even a cessation of emissions today would allow continuing destruction of the ozone layer for decades. Furthermore, CFC's migrate slowly from the point of emission to the upper atmosphere where they work their destructive havoc. Today's emissions of CFC's will not begin to destroy the ozone layer for many years, and a reduction in emissions will not abate that destruction for a similar time period. Thus we must adopt control policies in anticipation of harm that is not predicted to occur for a much longer time than the time span thought to motivate the political system. This raises the question whether we can act before it is too late.

The long time lags required for environmental improvement to result from reduced discharges of greenhouse gases mean that large reductions in emissions may be necessary even to stabilize environmental quality. The fifty per cent reduction in CFC emissions agreed to in the Montreal Protocol may be seriously inadequate, and there are demands for reductions of 90 per cent or more even to ensure that 50 years from now the ozone layer has been stabilized. Canada's commitment to a 50 per cent reduction in acid gas emissions by 1994 is regarded as an important step, but not a complete solution to the acid rain problem. And while some uncertainty remains about the ultimate effects of carbon dioxide emission reductions, it seems clear that dramatic reductions from current emission rates would be necessary if we hope to stabilize the environmental CO_2 concentration. In short, we can expect demands for discharge reductions of global pollutants ranging from 50 per cent to 90 per cent, and in the case of CFC's, perhaps 100 per cent.

III. Current Environmental Policies

Traditional environmental policies were designed to deal with local pollution concentrations, not with global pollution problems. In the United States, the approach to non-toxic pollutants has been to set ambient air quality criteria which specify allowable atmospheric concentrations of the pollutant, and then to develop emission regulations which will achieve these ambient concentrations. Initially, ambient air quality goals could be achieved by dispersing pollutants over a wider area, and throughout North America, during the 1960s and 1970's, tall stacks were built to disperse air pollution over a wider area in order to reduce local demands for control and to comply with regulations specifying ambient concentrations. Tall stacks, of course, do nothing to reduce the total amount of pollution discharged. Criteria pollutants currently include sulphur dioxide, nitrogen oxides and ozone, but not methane, water vapour, or CFC's. Titenberg (1988, p. 366) concludes "it has become painfully clear in the United States that the Clean Air Act is ill-suited to solve regional pollution problems". There is as yet no policy directed toward carbon dioxide emissions in the United States or in Canada. The U.S. approach to acid rain so far has included requiring scrubbers on new power plants and conducting research. The EPA has vigorously pursued chlorofluorocarbons pursuant to the Montreal Convention, and has adopted regulations limiting their use and allocating production rights to individual firms.

In Canada, also, the primary thrust of legislation has been to protect local rather than global environments. The application of the Ontario EPA, for example, has generally limited discharges that cause local harm to the environment. Regulation 308 under the EPA lists allowable ambient concentrations for many pollutants, thereby allowing greater emissions from taller stacks, because of increased dispersion. Thus in Canada as in the United States, environmental policies of the 1970's and much of the 1980's primarily tackled high concentrations of pollution and not total emissions.

IV. Possible Future Environmental Policies

While the EPA's action under the Montreal Protocol may be a step toward a satisfactory CFC control policy, there has been no action on carbon dioxide. The current state of public concern however has generated fully 10 legislative proposals in the United States, and several studies suggesting policies for dealing with global warming. A brief review of these proposals is instructive.

A. Studies of Policy Options

During 1988, U.S. senators Wirth and Heinz sponsored a study "Project 88" that assembled a set of recommendations for environmental policies designed for the incoming president, whoever he might be. (Stavins, 1988.) With respect to greenhouse gases, Project 88 recommends research and development on control technologies and adaptation strategies. It recommends promoting energy efficiency in the development of alternative fuels, and promoting the prevention of deforestation. Its novel policy proposal is that new sources of greenhouse gases be required to secure emission permits representing offsetting emission reductions from existing sources. A national market for CO_2 emission offsets is proposed. This program is said to ensure that CO_2 emissions would stabilize at current emission rates. However, it is not clear how the policy would work for mobile sources, in contrast to major stationary sources.

In February 1989 the U.S. EPA presented to Congress a draft report "Policy Options for Stabilizing Global Climate". (EPA, 1989.) EPA identified the emission reductions required for each of a set of greenhouse gases in order ultimately to stabilize atmospheric concentrations, displayed in Table 1: 50 per cent to 80 per cent for carbon dioxide, 75 per cent to 100 per cent for CFC's and a freeze on emissions of oxides of nitrogen. Actions that might be adopted in North America and/or elsewhere to reduce greenhouse gas emissions include: improving new automobile fuel economy; reducing automotive emissions to U.S. rates in the rest of the world; improving home insulation and home heating efficiency; eliminating net global deforestation; phasing out CFC's; imposing carbon emission fees and/or production fees on coal, oil, and natural gas and pursuing R&D on solar technology. This report states that energy conservation would be an important element in reducing carbon dioxide emissions, and that many methods of energy conservation are currently cost effective but not employed. The report does not perform the economic modelling necessary to determine the pace at which energy conserving technologies would actually be adopted, nor does it really define how a government would cause them to be adopted. However it does project the CO_2 reductions that might result from various policy combinations, and the "Rapid Reduction" scenario relies heavily on large fees to discourage carbon burning. The report seems optimistic in its faith both in the performance of new technology for energy conservation and in the willingness of consumers to embrace that technology. I do not believe that the policies identified in this report would come close to achieving the 50 to 80 per cent reduction in carbon dioxide emissions that would be required merely to stabilize global climate early in the next century unless carbon emission fees caused the price of consuming fossil fuels to rise far above present levels. There is no indication from recent experience that more efficient technologies will be more widely used without significant economic pressures such as those arising from large increases in energy prices.

The latest Worldwatch Institute report deals extensively with global pollutants and global warming. It recommends a variety of changes in both technology and lifestyle, but the central solution is improved energy efficiency, which is said often to be cost-effective at present energy prices. Like other reports, this one grapples more successfully with technology than with policy, but it does suggest a carbon tax, along with energy efficiency standards. (Worldwatch, 1989, p. 179)

Two Canadian reports are relevant. The Federal government was presented with a "Greenprint for Canada" in 1989, prepared by a coalition of environmental groups. (Greenprint, 1989) With respect to the global environment, it recommends pursuing a 20 percent CO_2 reduction from 1988 levels by 2005 through tough automotive and energy efficiency standards, a more energy-efficient building code, promoting transit and railroads, introducing a carbon tax that would raise $40 billion over 15 years, and abandoning subsidies to energy and resource industries. The second report was presented to a task force of Federal and Provincial energy ministers at the end of the summer of 1989. (DPA, 1989.) This report projects a 50% growth in CO_2 emissions by the year 2005 in the baseline scenario. See Table 2. It classifies control technology as: market penetration, which would be adopted in response to market forces; measures economically attractive to society (MEAS), for which social benefits exceed social costs; and measures that are technologically feasible. Engineering analysis is used to determine the reductions in CO_2 emissions using each technology category. The report concludes that the maximum technologically feasible reduction will achieve a 20% emission reduction by 2005, but that MEAS technology falls somewhat short of this goal. Market penetration technology achieves very modest reductions. This implies that the goal of the Toronto Conference is technologically achievable, but would be very difficult to achieve.

B. Legislative Initiatives, United States

While the bills introduced in congress dealing with global warming differ in detail, some characteristics appear in a number of them. HR1078 is widely supported (with over 50 sponsors) and represents one of the more ambitious pieces of legislation. It sets as a national goal a reduction in the discharge of carbon dioxide in the United States from 1988 levels by at least 20 per cent by the year 2000.[1] Other goals include minimizing the cost of achieving national energy needs while reducing carbon dioxide emissions, and promoting international agreements to achieve similar reductions worldwide. The thrust of the bill is to promote energy efficiency in buildings and community systems, in industry, in transportation, and in other sectors. Hundreds of millions of dollars a year for research and development are proposed.[2] Energy efficiency standards are to be set for appliances, energy efficient labels developed for windows, and studies are to be undertaken to examine opportunities for low energy transporation such as walking and bicycling. Expenditures are authorized for the implementation of a variety of energy conservation programs. A vigorous set of fuel economy standards for automobiles is proposed, extending the current Corporate Average Fuel Economy (CAFE) system to the year 2005, by which time a U.S. fuel economy rating of 38 miles per gallon should be achieved. Expenditures are authorized for a wide variety of alternative energy and renewable energy systems. While this bill proposes to spend large amounts of money on studies and programs, it has little to push consumers toward energy conservation. There is no limit on carbon dioxide emissions, no tax on fossil fuels or their use. It would be astonishing if this legislation by itself were to achieve more than a slight reduction from the base case increase in carbon dioxide emissions by the turn of the century. It would not come close to achieving its stated goal of a 20 per cent reduction. Other bills promote studies of clean coal programs and, global warming, and are aimed at reducing deforestation and encouraging reforestation. All are devoid of serious limits on CO_2 production. While Canadian environmentalists may lament that Canadian legislation lags behind that in the United States, perhaps they should take some comfort in the lower Canadian level of wishful thinking.

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[1] HR1078, section 3(a)(1).

C. Effective Policies

While the variety of policies discussed above might facilitate reductions in CO_2 emissions, none of them seems likely to ensure such reductions. Much reliance is placed on the gains from improved automobile fuel economy induced by tough new-car fuel economy standards, yet the existing CAFE program in the United States has serious deficiencies. Crandall and Graham's (1989) analysis of CAFE suggests that most improvements in automobile fuel economy were achieved as a result of high prices before the regulatory constraints became binding. If oil (and gasoline) prices remain at their current low levels,[3] it seems implausible that far more stringent CAFE standards can be imposed on auto manufacturers, or accepted by the motoring public. Worse, those standards do not apply to all vehicles, and if there is a mismatch between fuel prices and vehicle design resulting from fuel economy standards, buyers will shift to less regulated vehicles, moving from automobiles to light trucks, and from light trucks to goodness knows what. Furthermore, fuel economy standards do not reduce the amount of driving, nor induce consumers to use their most efficient rather than their least efficient vehicle. Finally, the fuel economy improvements from 1975 to 1985 were facilitated by downsizing bloated and inefficient North American vehicles without sacrificing useful carrying capacity.

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[2] HR1078, II, section 202.

[3] U.S. gasoline prices are now almost down to their 1971 levels after adjusting for inflation.

Now that the fat is gone, further reductions will be much more painful. Efficiency standards without higher energy prices will not achieve substantial energy savings.

With respect to non-transportation energy consumption, it seems likely that regulating appliance efficiency or building standards may reduce fossil fuel consumption somewhat. However no regulation can attract attention and stimulate action on all feasible means of energy conservation, including changing behaviour as well as technology, without the assistance of major increases in energy prices.

If it is desired to reduce carbon dioxide emissions substantially, it will be necessary to set limits on total emissions by issuing emission rights, or to impose a charge for those emissions. I see no possibility of any serious attack on global warming that does not incorporate marketable emission rights and/or effluent charges.

Consider first the use of emission rights. Acid rain policy provides some guidance in the implementation of emission rights. Ontario's "Countdown Acid Rain" programme has led the way in adopting source-specific annual total emission rights for the four major corporate sources of sulphur dioxide. It remains only to allow these rights to be bought and sold among sources for a regional marketable emission rights system to be in place. President Bush's proposal for acid rain controls in the United States specifies total discharges on an annual basis for several regions in the country and allows trading of emission rights among the major sources in a way that would ensure emission reductions over a period of time, yet ensure that reductions were achieved at the lowest possible cost.[4]

In the case of carbon dioxide, regulating individual sources or even groups of sources seems less promising, since the primary means of reduction will be through reducing fossil fuel combustion or switching fuels. Unlike sulphur oxides, there are millions of sources of CO_2 in Canada, including all motor vehicles, all fossil-fueled domestic heating and hot water heating plants, and many commercial and industrial consumers of fossil fuels that would have to be controlled to achieve significant pollution reductions. It is not clear how an emissions trading program would work for such a large number of diverse sources. Indeed, it is not clear that it could be applied to motor vehicles at all. In this case, a tax on the carbon content of the fuel seems to be the most straightforward approach, and perhaps the only feasible one. I conclude that an effective carbon dioxide policy must include a substantial tax on the carbon content of all fossil fuels that are burned.

How large must the tax be? By 2005, a 20% reduction from 1988 levels means almost a 50% reduction from the base case 2005 levels.

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[4] See Titenberg (1985) for a thorough discussion of the emission rights concept.

(DPA, 1989, p. ES3.) The demand for fossil fuels as a whole must have an elasticity of demand less than one,[5] meaning that to reduce consumption by 10% you need to raise the price by more than 10%. This implies that the tax must at least equal the current retail price of fossil fuels if the goal is to be met. That is, we need a 100% sales tax on coal, oil and natural gas if we hope to reduce emissions by 20% from 1988 levels early in the next century. The price of gasoline and diesel fuel must double. While projecting the result of such large price changes is highly uncertain, these estimates suggest the magnitude of the challenge. Proposing taxes in these amounts would make the GST look wildly popular by comparison. On the positive side, it would generate enormous revenues, contributing enormously to reducing the federal deficit.

A second element in a policy to reduce CO_2 emissions is an end to subsidies for fossil fuel production. Investing public funds in energy megaprojects such as Hibernia, tar sands plants, and arctic energy production or transportation is contrary to efforts to reduce consumption of fossil fuels. These projects should proceed only when the market says that they are economical. Provincial subsidies of electricity through guarantees of Hydro bonds should also be eliminated. Once again, good environmental policy is good for the public purse.

V. Effects of Policies on Energy Consumption and Trade

A. Effects on Energy Consumption

The primary qualitative impacts of the proposed carbon tax are easy to trace. The implicit cost of burning fossil fuels will increase, with the largest increase for coal, a lesser increase for oil and a smaller increase for natural gas. In addition to the increase in the cost of burning these primary fuels, there will be a direct increase in the cost of most electricity, in proportion to the carbon content of the fuel used to generate it.

The increased cost of burning fossil fuels and the increase in the price of electricity will reduce energy consumption generally. These reductions will be achieved through a variety of measures including conservation by the end user, co-generation, and a host of technology and lifestyle changes. As these price increases and demand reductions feed back to primary sources, they should result in a shift in demand from coal to oil and from oil to gas. For electricity generation there may even be a shift from natural gas to nuclear energy, at least in Canada where the nuclear option has not been written off. Electricity consumption may decrease, on the assumption that conservation by end users will offset substitution of electricity for fossil fuels.

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[5] See, Bohi (1981); Pindyck (1979); Griffin (1979); and Hogan (1988). While the elasticity estimates vary widely, taken together, they suggest that the aggregate fossil fuel elasticity would be less than 1.0.

The direction of the changes indicated above can be expressed with some confidence. The magnitude of the changes however would require careful estimation using comprehensive energy demand models. It is anticipated, at least by the EPA, that new technologies would play a major role in energy conservation during the 1990s if substantial CO_2 reductions are to be achieved. While historically estimated models are not very helpful for simulating future technology changes, at least we have had fifteen years experience with responses to OPEC crisis of 1973. We are therefore in a far better position to predict the effects of increases in fossil fuel costs today then we were in the early 1970's.

B. Effect on Trade

If a carbon tax doubled the price of fossil fuels in Canada alone, relative prices of energy and energy-intensive goods would be quite different in Canada and in the U.S., seriously distorting trade in those goods. Before Canada adopted such a tax alone it should carefully study the likely economic effects and seriously consider how to deal with the trade flows that would result. But Canada cannot solve the CO_2 problem alone, so such a policy would more likely be adopted at least in concert with the United States, and perhaps jointly by many OECD countries. Some will argue that even if adopted internationally, such a tax would cripple important segments of Canadian and U.S. industry. In general, this proposition is dubious. The revenues generated by such a carbon tax would be enormous. These revenues could be used to reduce other taxes that presently impose burdens on Canadian consumers and industry. While substituting a new tax for an old tax has distributional consequences, it will not make Canada generally less competitive. The sector most directly impacted would be coal producers, who would see substantial declines in their markets if the policy is effective. Oil demand will decrease. Another significantly affected sector would be electric utilities, which face only modest foreign competition, and would not likely lose market share to fossil fuels in the face of the proposed policies. But few other sectors of the North American economy are likely to suffer seriously.

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TABLE 1

Greenhouse Gas Emission Reductions To Stabilize Atmospheric Concentrations at Current Levels

Gas	Reduction Required
Carbon Dioxide	50-80%
Methane	10-20%
Nitrous Oxide	80-85%
Chlorofluorocarbons	75-100%
CO, NO_x	Freeze

Source: EPA (1989, p. 15 Table 1)

TABLE 2

Projected Carbon Dioxide Emissions: Canada
(Millions of Tonnes of CO_2 Annually)

	1988	2005	1988-2005 Growth
Residential Sector	53	61	15%
Commercial Sector	32	49	53%
Industrial Sector	121	163	35%
Transportation Sector	128	180	40%
Electricity Generation	85	174	104%
Total	419	627	50%

Source: DPA (1989, p. 10)

TABLE 3

Estimated Direct Carbon Dioxide Emission Reductions Achievable[1]: Canada (Millions of Tonnes Annually by 2005)

	Market Penetration	Measures Economically Attractive to Society[2]	Technical Potential[3]
Residential	3	10	20
Multi-Residential	2	4	6
Commercial	4	12	25
Industrial	5	9	40
Transportation	18	68	87
TOTAL	31	103	177

NOTES:

1. Fossil fuel use in the sector.
2. Includes measures that are economically attractive from society's perspective and that form part of the technical potential.
3. Technical potential includes all measures that are technically feasible in a sector to reduce direct carbon dioxide emissions.

Source: DPA (1989, p. 32.)

VOLUME I
SESSION A
AIR QUALITY RESEARCH
VERBAL PRESENTATIONS

A2

Chemical transformation of a pollutant by two competing pathways:

Photolysis by sunlight and hydroxyl radical attack

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Abstract

At last year's conference, we reported laboratory data on the photochemical behaviour of chlorinated phenols in the gas phase. These compounds can undergo chemical transformation in the troposphere by two distinct mechanisms: direct photolysis by sunlight, and attack by hydroxyl radicals. The present work has been directed to obtaining estimates of the rates of each of these processes in the troposphere.

The rate of direct photolysis can be calculated from the tropospheric solar spectrum, the absorption characteristics of the substrate, and the quantum yield of photolysis. To calculate the rate of reaction of a substrate with the hydroxyl radical, we make use of the recent (1988) observations of Platt et al. that the concentration of OH is proportional to the rate of photolysis of ozone, which is itself calculated analogously to the rate of direct photolysis of the pollutant.

Calculations have been made for several chlorinated phenols, for which both reaction channels are of comparable importance and where the tropospheric lifetime is of the order of days. A lifetime of this magnitude implies that the tropospheric lifetime varies greatly with geographical location and season. For very long lived compounds such as the chlorofluorocarbons, the calculation has been developed so as to obtain globally and seasonally averaged results.

Introduction

We have developed a computer model for estimating the rate of chemical transformation of a tropospheric constituent when two reaction channels are available: direct solar photolysis and attack by hydroxyl radicals. The model is executable on an office microcomputer using commercially available spreadsheet software. It is semi-empirical rather than being derived totally from first principles, in that it uses the recent observations of Platt et al. (1988) that the concentration of hydroxyl radicals in the troposphere appears to depend linearly upon the rate of photolysis of ozone, eq. [1].

[1] $[OH] = \text{Constant} \times [O_3] \times (\text{Flux of photons able to photolyze } O_3)$

The constant in eq. [1] is obtained empirically from the data reported by Platt et al.; all other quantities can be calculated with the aid of experimental data as follows.

For hydroxyl radical attack:

The zenith angle of the Sun may be calculated for any geographical location, date, and hour of the day. Tabulations of the distribution of tropospheric intensities vs. wavelength are available (Finlayson-Pitts and Pitts, 1986). For weak absorption, the rate of photolysis of ozone $J(O_3)_\lambda$ at any wavelength is given by equation [2].

[2] $J(O_3)_\lambda = I_\lambda \cdot \sigma_\lambda \cdot \phi_\lambda \cdot [O_3]$

I_λ, the solar intensity at a given wavelength and zenith angle, ϕ_λ, the quantum yield for ozone photolysis at different wavelength, and σ_λ, the absorption cross section for ozone, are all tabulated. The product $(I \times \sigma \times \phi)_\lambda$ is the rate constant for photolysis of O_3 to O^* at any wavelength. At any time of the day, i.e., at each zenith angle, the term $(I \times \sigma \times \phi)_\lambda$ must be summed over the wavelength range 290 - 325 to obtain the overall photolytic rate constant $(I \times \sigma \times \phi)_Z$. Estimates for $(I \times \sigma \times \phi)_Z$ at zenith angles in between those found in the tables are found by fitting to a cosine function, eq. [3], in which 'm' is an adjustable parameter whose value is usually about 2.4.

[3] $(I \times \sigma \times \phi)_Z = (I \times \sigma \times \phi)_{Z=0} \cdot (\cos Z)_m$

Using eq. [1] to obtain the hydroxyl radical concentration from the rate of photolysis of ozone, the rate of reaction of OH with the substrate is found from the second order rate equation, eq. [4], using known or estimated (Zetsch, 1982) values of the second order rate constant.

[4] $\text{rate} = k.[OH].[\text{Substrate}]$

For the direct solar photolysis:

The rate of photolysis of the substrate may be calculated analogously to the rate of photolysis of ozone. The data required are the solar intensity at each wavelength for a given zenith angle, together with the absorption cross section for the photochemically active substance as a function of wavelength, and the quantum yield for photolysis, assumed for simplicity to be independent of wavelength. For weak absorption, the rate of photolysis of a substrate per unit area, $J(\text{substrate})_\lambda$, at each wavelength is given by equation [5].

[5] $J(\text{Substrate})_\lambda = I_\lambda(2.303\,\epsilon_\lambda\,\phi[\text{Substrate}]) = (I_\lambda\,\sigma_\lambda)\,\phi[\text{Substrate}]$

Estimates for $(I \times \sigma \times \phi)_Z$ at zenith angles in between those found in the tables are again obtained by fitting to a cosine function analogous to eq. [3]. If, experimentally, molar absorptivities (ϵ_λ, units L mol^{-1} cm^{-1}, to a logarithmic base of 10) are available rather than absorption cross sections, the conversion is $\sigma = (3.824 \times 10^{-21}) \times \epsilon$. The total rate of photolysis is found by summing eq. [5] over all wavelengths where the substrate absorbs.

In work submitted for publication (Bunce et al., 1989), we described the development of the model, and applied it to the example of pentachlorophenol in the troposphere. Substantial differences in the rate of reaction were found according to the geographical location and season that was modelled. For this particular substance, the rates of reaction by each reaction channel are comparable, although large zenith angles favour the direct photolysis somewhat. This is because the absorption spectrum of pentachlorophenol extends out to longer wavelengths than that of ozone, and it is the shorter wavelengths of UV-B radiation which are the most attenuated at large zenith angles. We now report the application of the model first, to a range of chlorinated aromatic air pollutants and second, to the study of substances having extremely long atmospheric lifetimes.

Chlorinated aromatic compounds

We have investigated members of the chlorobenzene, chlorophenol, and chlorobiphenyl series. The first set of calculations was carried out for the location Toronto, Ontario, 43.70 °N, 79.47 °W. Figure 1 shows a typical set of results, for the case of 2,4-dichlorophenol. The six curves represent the loss of 2,4-dichlorophenol over a 4 day (i.e., 96 h) period for the six dates (top to bottom) December 21, January 21, February 21, March 21, April 21, and May 21; in each case the initial concentration of dichlorophenol was 1.0 ng m^{-3}, and there was assumed to be no replenishment of the material initially present. At the winter solstice, the loss of substrate is less than 5% per day, and this increases by an order of magnitude as midsummer approaches. As expected, the calculation shows the rate of substrate loss to change most rapidly near the time of the equinox. The flat portions of each curve represent the hours of darkness. No loss of substrate is predicted during these hours, because both solar photolysis and hydroxyl radical attack are photochemical reactions; the first is directly photochemical, and the second is indirectly photochemical because OH is produced through ozone photolysis. Because OH is so reactive, it has a short lifetime, and so its concentration goes to zero after darkness falls.

Around March 21, the calculated concentration of 2,4-dichlorophenol after four days is close to 1/e (37%) of its initial value, and one could therefore reasonably state that the lifetime of 2,4-dichlorophenol with respect to chemical transformation is expected to be about 4 days under these conditions. However, the loss of substrate does not occur continuously with time, and so it is not strictly accurate to describe 2,4-dichlorophenol as disappearing with a rate constant of 0.25 day^{-1}. Like the reaction rate, the rate constant varies continuously through the day, and 0.25 day^{-1} is a weighted average, for which we will use the symbol "k" through this paper. All values of "k" were obtained by determining the percent loss of substrate at the end of 1 day, since if x% of substrate remains after 1 day, then eq. [6] is the integrated form of a (pseudo)-first order rate expression.

[6] $\ln (x/100) = -\text{"k"}.(1\ \text{day})$

Numerically, "k" = $\ln (100/x)$ day^{-1}, and the tropospheric lifetime estimate is 1/"k" days. At Toronto, the tropospheric lifetime of 2,4-dichlorophenol varies from about 2 to 20 days, depending on the season. Conversely, at a series of latitudes 0 to 90 °N on the same date (March 21) the tropospheric lifetime estimate varies from 1.7 to several hundred days. These results emphasise the importance of using appropriate information concerning geographical location and season to model the chemistry of an atmospheric constituent.

When the atmospheric lifetime is short (days), the parameters appropriate for the particular geographical location and season must be used, because the chemistry takes place on such a short time scale that the substance will not have been transported far from where it was emitted: i.e., the original geographical coordinates can be used throughout the calculation. Calculations were carried out for several other chlorinated aromatic compounds, including substances that react principally with OH (e.g., 1,2,4-trichlorobenzene), and others whose major reaction channel is photochemical (e.g., pentachlorophenol). All these compounds were calculated to have tropospheric lifetimes for chemical transformation of a few days, and so the same geograhical coordinates were used throughout the calculations.

A different approach must be used for substances which become globally dispersed. The use of fixed geographical coordinates corresponding to the emission location is now unrealistic, and globally and seasonally averged information is more appropriate. In order to test the model under quite different conditions, calculations were carried out for several substances which are very unreactive in the atmosphere. The first of these was 1,1,1-trichloroethane, since this has been used in other studies to estimate the globally and seasonally averaged concentraion of OH. In the troposphere, trichloroethane does not absorb sunlight and thus is transformed chemically only by reaction with OH. The rate constant 1.19×10^{-14} cm^3 $molecule^{-1}$ s^{-1} is taken from Prinn et al. (1987).

A globally and seasonally averaged [OH] was obtained by carrying out the following calculation once for each season of the year. Recall that the model permits [OH] to be calculated at fixed location and time of day; the average over the day is calculable because [OH] is continuously recalculated through the day. In principle the global average for the date in question is found by obtaining the above information at all latitudes and averaging. There is the slight complication that the length (L) of a circle of latitude depends on the latitude, as shown in eq. [6], where R is the radius of the Earth and θ is the latitude.

[6] $L = 2\pi R.\cos\theta$

Hence a band around the Earth having width $\Delta\theta$ has area $2\pi R^2.\cos\theta.\Delta\theta$. Consequently, the globally averaged concentration of OH is calculated by eq. [7], where n is the number of bands evaluated for $-\pi/2 < \theta < \pi/2$.

[7] Annual average $[OH] = \Sigma(\Sigma [OH]_{local}.\cos\theta.\Delta\theta/2)/n$

The annual average is deduced to be near 1×10^6 radicals per cm^3, which compares with the estimate by Prinn et al. of 7.7×10^5 radicals per cm^3. We note that the consequence of the different lengths of a circle of latitude is that most of the OH in the troposphere is located at low latitudes. Thus the rate attack by OH (and equally of photolysis) of a globally distributed pollutant is determined mostly by the solar flux at small values of latitude.

Reasonable agreement is thus obtained for the globally and seasonally averaged [OH] between other estimates and the present calculation, even though we have not taken into account any global variation in the tropospheric concentration of ozone (recall that the concentration of ozone directly affects the calculated concentration of OH in our model).

We have obtained estimates of the tropospheric lifetimes of several long-lived haloalkanes, all of which also react exclusively by hydroxyl radical attack. Two methods were used: (1) using the globally and seasonally-averaged OH concentration from Table 4; (2) calculating the daily loss of substrate at low latitude (23 °) on March 21, and taking this to be representative of the year. The compounds selected for this study were methane, CFC-12, CFC-22, and CFC-134a. CFC-12 (dichlorodifluoromethane) is a "hard" CFC which is covered by the "Montreal Protocol on substances that deplete the ozone layer". CFC-134a (1,1,1,2-tetrafluoroethane) is the leading contender for a replacement for CFC-12 in refrigerators; it contains no chlorine and hence has no ozone depleting potential. CFC-22 (dichlorofluoromethane) is reported to have 5% of the ozone depleting potential of $CFCl_3$, which it is quickly replacing as a foam blowing agent. Because of its C-H bond, it reacts more rapidly with OH than $CFCl_3$. The present estimates on the tropospheric lifetimes of these compounds accord well with previous assessments.

The present work has shown that the simple model which we previously described can give useful estimates of tropospheric lifetimes for both short and long-lived compounds. However, this model would be inappropriate for a substance such as SO_2, for which a substantial proportion of the transformation occurs in aqueous droplets, rather than homogeneously in the gas phase.

We have given some thought to the question of whether the model can be refined so as to yield more precise lifetime estimates. We have decided against this on two counts. First, the environmentalist is usually concerned only about the general magnitude of the rate of transformation of an atmospheric pollutant. It is useful to know that the lifetime is 3 days rather than 3 weeks or 3 months, but largely immaterial whether it is 3 days or 4 days. Second, refinement of the model would necessitate providing files of parameters such as the temperature dependence of rate constants, diurnal temperature variation in the atmosphere, diurnal varaiation of ozone concentration etc. Provision of all these data would make impossible the original goal of our work: to provide a model simple enough that it could be executed on an office microcomputer using commercially available software. The virtue of the present model is in affording in a straight forward fashion an order-of-magnitude estimate of atmospheric reactivity.

Acknowledgements

Financial support by Environment Ontario (Air Resources Branch) is gratefully acknowledged.

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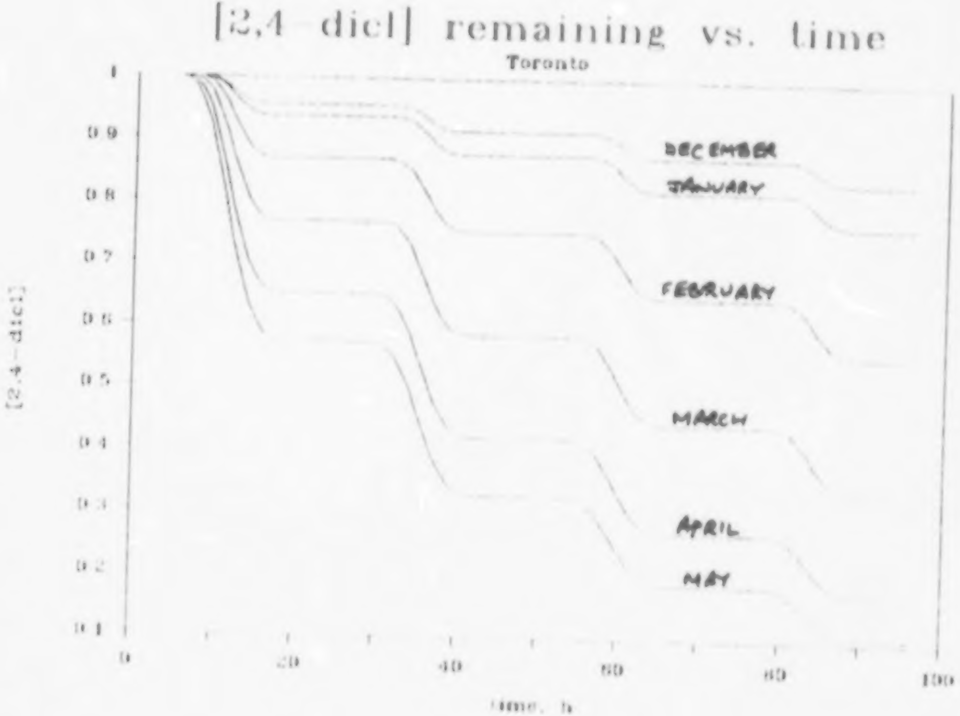

[2,4-dicl] remaining vs. time

A3

ATMOSPHERIC TRACE GAS MEASUREMENTS
USING A
TUNABLE DIODE LASER ABSORPTION SPECTROMETER

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INTRODUCTION

There are currently two state-of-the-science Eulerian models being used to simulate and study the chemistry of acid deposition and oxidant formation over North America. They are the Acid Deposition and Oxidants Model (ADOM), supported by the Ministry of the Environment, the Atmospheric Environment Service of Environment Canada, the Electric Power Research Institute (EPRI), and Umweltbundesamt (West Germany) and The Regional Acid Deposition Model (RADM) supported by the Environmental Protection Agency (EPA). These models include our best understanding of the sources of gases to the atmosphere, the best available three dimensional meteorology, the most complete gas and aqueous phase chemistry available, and our best measurements of trace gas concentrations. Realizing the importance of the predictions of these models, it was deemed necessary to establish their credibility by comparison with observation.

The Eulerian Model Evaluation Field Study (EMEFS) was designed to provide sufficient data to allow a full evaluation of the models. The Canadian component of the study involved data collection from the MOE-APIOS and AES-CAPMoN networks. In addition, two sites were designated as intensive or enhanced sites. These were the AES site at Egbert (near Barrie) and the Ministry site at Dorset. The purpose of these sites was to obtain data using enhanced techniques that required operation by specially trained personnel or at a frequency not possible under normal operating conditions.

While the field study was put in place for model evaluation it became clear that the data obtained, especially that from the enhanced sites, could also be used to address a number of additional issues. The Canadian Institute for Research in Atmospheric Chemistry (CIRAC) took the lead in the co-ordination of the Canadian Air Chemistry Experiment which aimed to ensure the collection of a complete data set capable of addressing some specific atmospheric chemistry questions.

The first stage of this study was undertaken in the summer of 1988 with measurements being taken at the following surface sites: Dorset; Egbert; upstate New York (Whiteface Mountain);

Illinois (Bondtown); Georgia (Brasstown Bald); Pennsylvania (Scotia); and Virginia (Whitetop Mountain). Measurements were also made from five aircraft including two Canadian aircraft flying between Dorset and Egbert. This data is now analyzed and several papers on the regional distribution of the reactive species are being prepared.

This group's contribution to this program centred around the Tunable diode laser absorption spectrometer (TDLAS), which was used to measure the concentrations of formaldehyde and hydrogen peroxide at the Ministry site at Dorset. Formaldehyde is an intermediate in the atmospheric oxidation of hydrocarbons and hydrogen peroxide is a product of radical-radical recombination. These species have very short atmospheric lifetimes and so the prediction of their concentrations by the models will be sensitive to the chemistry used in the model. Measurements of the concentrations of these molecules therefore will provide a stringent test of the models. Currently the TDLAS is the only technique available to measure both of these species.

In addition to formaldehyde and hydrogen peroxide we measured NO_x, NO_2, O_3, temperature, humidity, wind speed, wind direction, and solar radiation. In the summer of 1989 we returned to Dorset to collect additional data to improve the database for the site. A collaborative effort with Dr. Niki and Ontario Hydro allowed a study on the movement of the nocturnal boundary layer, a detailed hydrocarbon inventory as well as an extension and improvement to the 1988 data-base.

The data analysis for this summer is still underway so this paper will concentrate on the results from the summer of 1988.

RESULTS: The period July 31 to August 7 1988.

The most notable event to reach Dorset during the measurement period occurred from August 1 to August 5. During this period the whole of Northeastern North America was subjected to an almost stationary high pressure system. This system was characterized by low winds and high temperatures (see Figure 1) and produced a slow flow of air from the south to the Dorset site. This slow air movement resulted in very high concentrations of primary and secondary pollutants. The data collected during this event are shown in Figures 1 to 5, including the day before and the day after the event. Figure 2 shows the solar UV irradiance for this period with the midday maximum for the period is shown as the horizontal line. The irradiance showed a lower maximum than observed for clean days due to the presence of haze, both water and particulate. The cloudy nature of the period is also clearly visible.

The NO_x concentration for the period is shown in Figure 3. The concentration was about 2 ppbv prior to the event. Concentrations of 2 to 3 ppbv seem to be typical of the summer

NO_x concentration in this area. On August 1 the NO_x concentration rose steadily during the day to a maximum at 2000 hrs. We do not believe that we see the local site traffic as there is no increase in the NO_x at 0830 and 1630 when the site personnel start and finish work. The NO_x reached a maximum value on August 2 but still stayed above the background until late on August 6.

Back trajectories for July 31, August 4, and August 7 are shown in Figure 6. They show that on July 31 the air came from the Northwest, presumably the clean direction. For August 3 to 5 the air was clearly from the industrial and populated areas to the south. On August 6 the trajectories began to move northward and by the August 7 the air was clearly originating northwest of the site.

Ozone and formaldehyde are secondary pollutants and should show similar behaviour. The data are presented in Figures 4 and 5 respectively. The first point to note is that the strong diurnal variation observed for ozone and formaldehyde is due to the presence of a strong nocturnal inversion. After sunset, typically at 2000 hrs, both the ozone and formaldehyde show steady decreases in concentration as the inversion forms and the reactive species are deposited to the surface thus depleting the lower layer which is only a few tens of meters deep. This inversion breaks up at around 0800 due to surface heating. This then allows the air from above the nocturnal layer to be mixed to the surface thus giving an increase in concentration at the surface. Thus only daytime data should be used in any examination of the chemistry.

The most marked change in daytime concentration was in ozone. On July 31 it was constant around 40 ppbv, a typical summer continental background concentration. However, after the incursion of air from the south, daytime maxima above 60 ppbv persisted until August 6 with August 7 showing an extremely low maximum of only 30 ppbv.

Formaldehyde measurements do not show as clear an onset of the event as does the ozone but the maximum concentration does correspond to the ozone maximum on August 2. The decrease in formaldehyde concentration from August 5 to August 6 is quite apparent in spite of the noisy signal.

The hydrogen peroxide concentration for this period was below the detection limit of the instrument, which varied from 0.3 to 1 ppbv.

RESULTS: Relationship between measured parameters

Examination of the relationship between the measured parameters can give information on the processes occurring in the atmosphere. Figure 7 shows the relationship between the ozone concentration and that of NO_x. Figure 8 is the same plot for the daytime data only. The improved correlation results from the removal of the low ozone data measured under the nocturnal inversion. This relationship is typical of that found at other rural sites.

Figure 9 shows the similar plot of formaldehyde against NO_x and Figure 10 the plot of formaldehyde against ozone, for the daytime only data. These show that formaldehyde is related to both these parameters and so must be produced by oxidation processes. The data also suggests a background formaldehyde concentration.

Thus the evidence is for the production of ozone and atmospheric oxidation either locally or in transit from the NO_x source region.

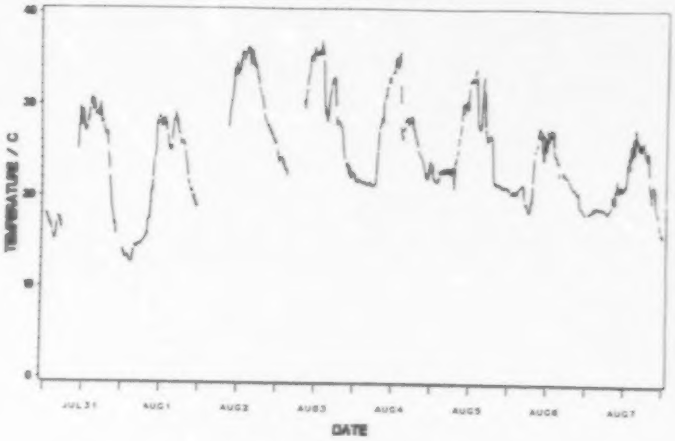
We are currently involved in a modelling effort to try and fully simulate this event.

CONCLUSION

We have measured the concentrations of formaldehyde, hydrogen peroxide, NO_x, NO_2, O_3, along with temperature, humidity, wind speed, wind direction, and solar radiation for two consecutive summers at the Ministry site at Dorset. Analysis of a major stagnation event shows the importance of high NO_x on the production of ozone and the importance of both NO_x and ozone on formaldehyde production.

ACKNOWLEDGEMENT

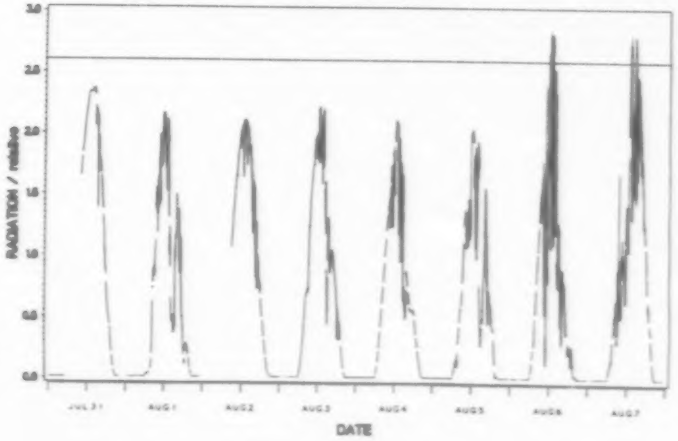
We wish to thank the Ministry of the Environment for their support of this project. We also thank the personnel at the Dorset site for their assistance.



TEMPERATURE
For JULY 31 to AUGUST 7

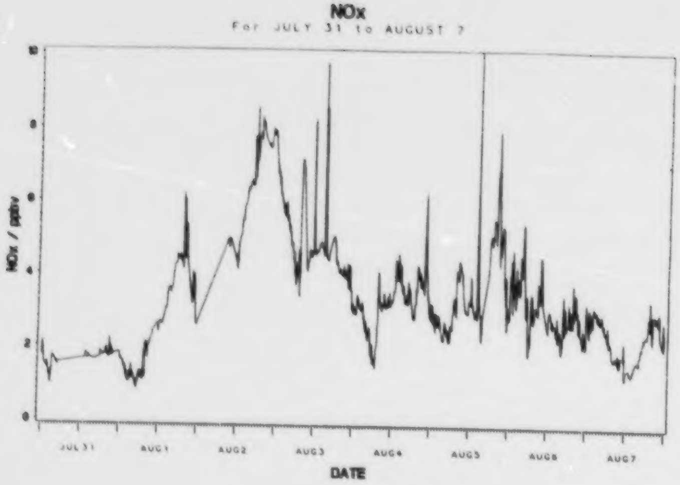
THE DATES ARE CENTRED ON LOCAL NOON

FIGURE 1 (UPPER) AND FIGURE 2 (BELOW)



SOLAR RADIATION
For JULY 31 to AUGUST 7

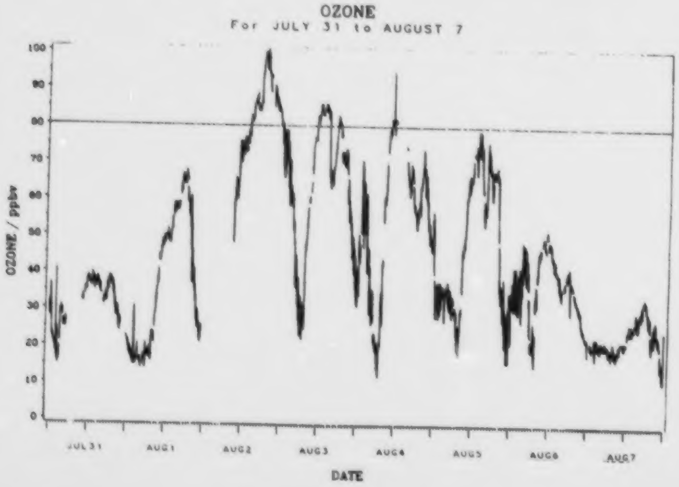
THE DATES ARE CENTRED ON LOCAL NOON


NOx

For JULY 31 to AUGUST 7

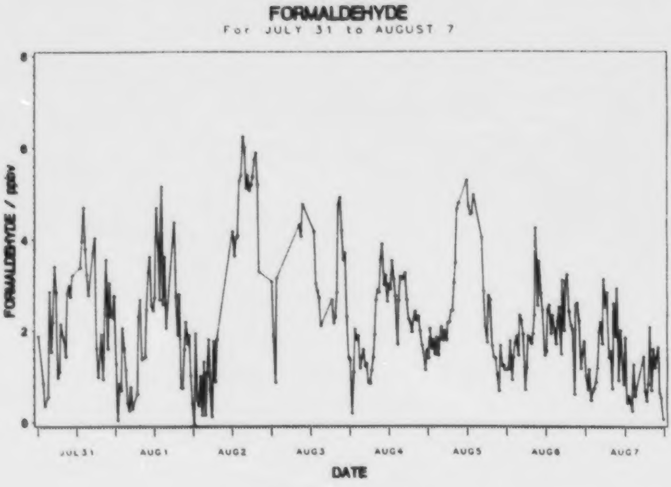
THE DATES ARE CENTRED ON LOCAL NOON

FIGURE 3 (UPPER) AND FIGURE 4 (BELOW)


OZONE

For JULY 31 to AUGUST 7

THE DATES ARE CENTRED ON LOCAL NOON



THE DATES ARE CENTRED ON LOCAL NOON

FIGURE 5

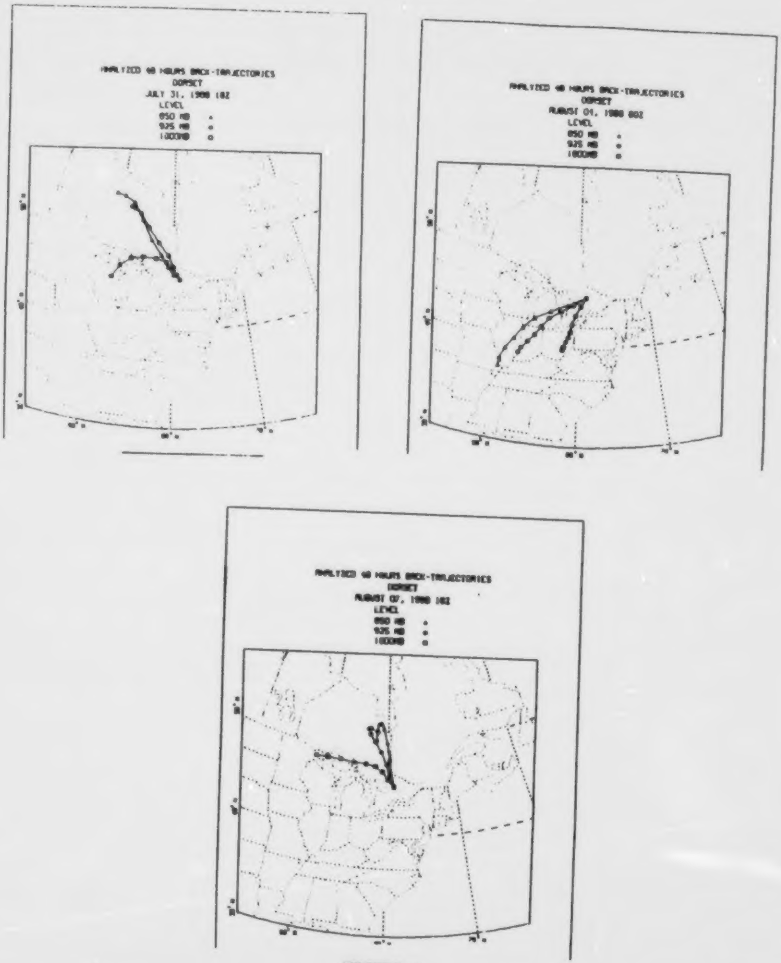

ANALYZED 48 HOURS BACK-TRAJECTORIES
DORSET
JULY 31, 1988 18Z
LEVEL
850 MB
925 MB
1000MB
ANALYZED 48 HOURS BACK-TRAJECTORIES
DORSET
AUGUST 04, 1988 00Z
LEVEL
850 MB
925 MB
1000MB
ANALYZED 48 HOURS BACK-TRAJECTORIES
DORSET
AUGUST 07, 1988 18Z
LEVEL
850 MB
925 MB
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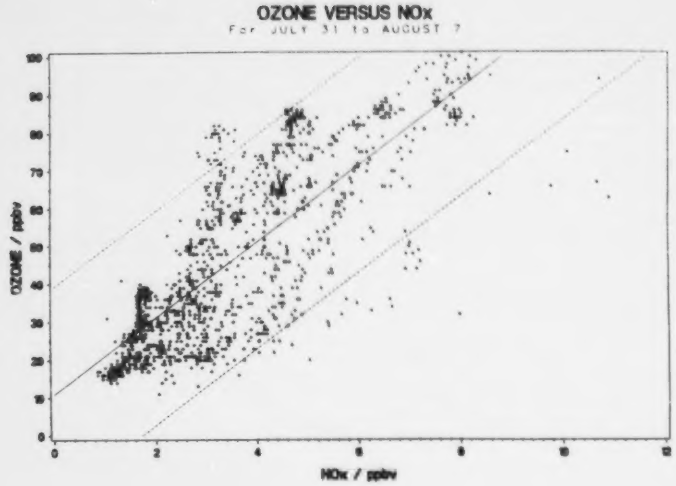
FIGURE 6

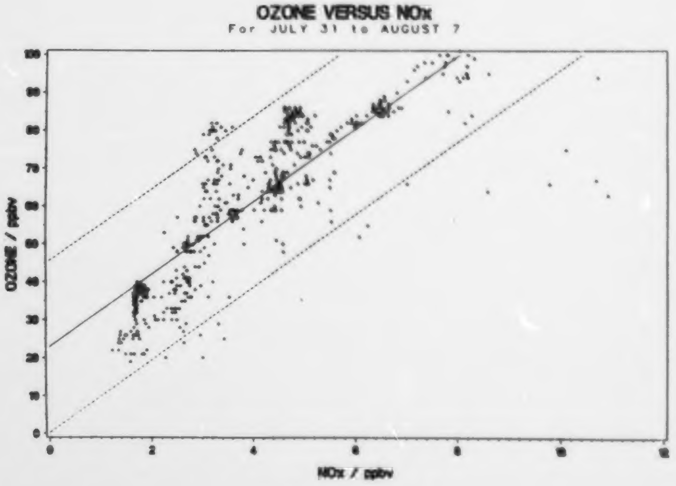


OZONE VERSUS NOx

For JULY 31 to AUGUST 7

ALL DATA

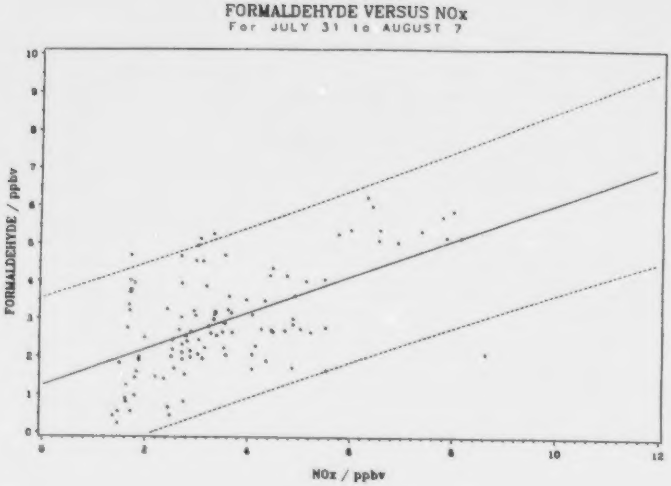
FIGURE 7 (UPPER) AND FIGURE 8 (BELOW)



OZONE VERSUS NOx

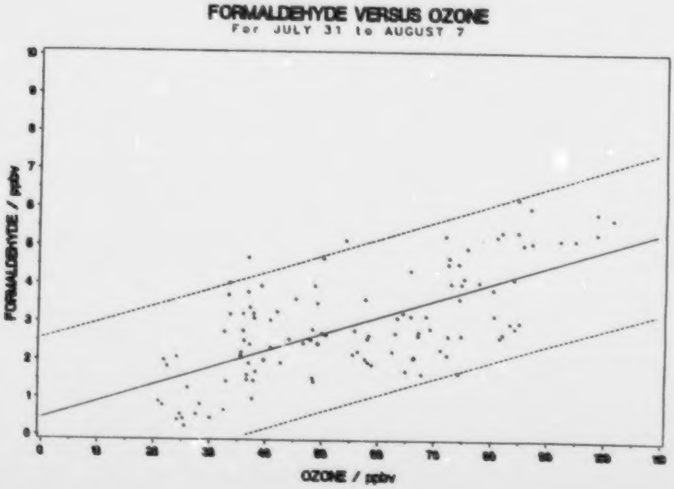
For JULY 31 to AUGUST 7

DATA BETWEEN 8am AND 5pm ONLY



DATA BETWEEN 10am AND 6pm ONLY

FIGURE 9 (UPPER) AND FIGURE 10 (BELOW)



DATA BETWEEN 10am AND 6pm ONLY

A4 DEVELOPMENT OF AMBIENT AIR MONITORING METHODOLOGIES FOR DIOXINS AND FURANS

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ABSTRACT

This program began in 1987 in recognition of the high public profile of dioxins and furans in the environment and the lack of an ambient air reference method for these compounds. Objectives of the work were to standardize sampling and analytical methods applicable to the determination of trace levels of dioxins and furans in ambient air; to document method performance; to assess the ability of commercial laboratories to successfully apply developed analytical procedures; and to develop a data base for dioxins and furans in ambient air. Results of ambient air monitoring for dioxins and furans carried out in Ontario are discussed. Results from an inter-laboratory round robin analytical methodology evaluation are also presented.

INTRODUCTION

Development of ambient air monitoring methodologies for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs) began in 1987 with direction from the Canadian Council of Resource and Environment Ministers' (now the Canadian Council of Environment Ministers) Working Group on Monitoring of Airborne Substances Excluding SO_x and NO_x. A three-year program was outlined to allow completion of a national reference method for dioxins and furans in ambient air, to determine the capability of Canadian laboratories to analyze these samples, and to transfer the technology to provincial, municipal, university, and private organizations.

The first part of this paper examines ambient levels of dioxins and furans measured at four sites in southwestern Ontario (Figure 1). Two sites (Windsor and Walpole Island) are operated under the auspices of the Environmental Protection Service of Environment Canada (EC) as part of the Detroit Incinerator Monitoring Program (Environment Canada, 1989). The Air Resources Branch of the Ontario Ministry of the Environment (MOE) also has a sampler at Windsor and operates two additional sites; one on Toronto Island as part of the Toronto Waterfront Remedial Action Plan, and the other in Dorset as a background site and for sampler development work.

In the second part of this paper, results of an inter-laboratory analytical method comparison are presented. Ambient air samples for this round robin study were collected at the Windsor site.

AMBIENT AIR LEVELS

A modified high volume sampler was used to draw air through a teflon-coated glass fibre filter upstream of a polyurethane foam (PUF) vapour trap. Sampling times varied between 24 hr and 72 hr yielding sampled volumes of 500 m^3 to 2000 m^3. Exposed samples were spiked with $^{13}C_{12}$-labelled PCDD surrogates and Soxhlet extracted with toluene. The extract was concentrated by rotary evaporation and worked up using a modified Dow clean-up. Samples were analyzed by GC/MS/MS on a Finnigan TSQ70 (MOE) or a Finnigan 4500 HRGC/LRMS (EC). Specific details of the sampling and analytical methodologies have been reported elsewhere (Tashiro, et al, 1989; Dann, et al, 1988).

There are no national air quality objectives for PCDDs or PCDFs, however, Ontario has a provisional ambient air guideline for 2,3,7,8-TCDD of 30 pg/m^3 annual average. Average values of T_4CDD, T_4CDF, total CDD, and total CDF from four sites in Southwestern Ontario are given in Table 1.

TABLE 1: Average Concentrations (pg/m^3) of Tetra and Total Dioxins and Furans From Four Sites in Southwestern Ontario.

WINDSOR (EC)

	$\bar{x}$	s.d	max	min	n
T_4CDD	—	—	ND	ND	13
T_4CDF	0.2	0.2	0.8	ND	13
Total CDD	2	2	7	0.4	13
Total CDF	0.4	0.4	1	ND	13

WALPOLE ISLAND

	$\bar{x}$	s.d	max	min	n
T_4CDD	—	—	ND	ND	7
T_4CDF	0.1[1]	—	0.1	ND	7
Total CDD	0.5	0.4	1	ND	7
Total CDF	0.1[1]	—	0.1	ND	7

WINDSOR (MOE)

	$\bar{x}$	s.d	max	min	n
T_4CDD	0.5	0.4	1	0.09	6
T_4CDF	0.7	0.3	1	0.3	6
Total CDD	4	4	11	1	6
Total CDF	2	1	4	1	6

DORSET

	$\bar{x}$	s.d	max	min	n
T_4CDD	0.1	0.05	0.2	0.08	5
T_4CDF	0.2	0.1	0.3	0.02	5
Total CDD	2	4	9	0.2	5
Total CDF	0.9	1	3	0.06	5

TORONTO ISLAND

	$\bar{x}$	s.d	max	min	n
T_4CDD	0.2	0.2	0.5	0.05	5
T_4CDF	0.4	0.4	1	0.02	5
Total CDD	2	1	4	0.9	5
Total CDF	1	1	3	0.4	5

NOTES:

All results to one significant figure
[1] Only one positive result
ND = Not Detected
Windsor (EC) 87•08 to 88•10
Windsor (MOE) 88•08 to 89•01

Of seven samples collected at Walpole Island, T_4CDD was not detected in any samples and only one sample yielded a positive result for T_4CDF and total CDF. Of the maximum values for total CDD reported for Windsor (MOE) and Dorset, O_8CDD accounts for 9 and 7 pg/m^3 respectively. The amount of T_4CDD and T_4CDF relative to total CDD and total CDF is shown in Figure 2. If the 2,3,7,8-substituted isomer accounted for all of the TCDD measured, ambient air levels at the sites sampled are well below the provincial provisional guideline.

Results reported here for Ontario are comparable to ambient air levels measured elsewhere in North America (e.g. Hunt and Maisel, 1989; Smith et al, 1989; Eitzer and Hites, 1987).

INTER-LABORATORY COMPARISON

Having established sampling protocols for dioxins and furans in air (Dann et al, 1988), the next stage was to determine the capability of private laboratories to analyze ambient air samples. Collocated samplers were installed at the Windsor site and ambient air samples were collected for analysis by each laboratory. Participating laboratories received the following: i) an exposed teflon-coated glass fibre filter (GFF) and polyurethane foam (PUF) plug; ii) a spiked extract consisting of combined extracts from collocated samplers; iii) a blank GFF and PUF plug; iv) a low level spiked blank (TCDD, HxCDD and OCDD spiked at 12, 20, and 29 pg/μL respectively) and iv) an unknown standard mixture. Laboratories were instructed to use their own methodologies.

The laboratories participating in the study included: Ontario Ministry of the Environment; Environment Canada; ELI ECO Laboratories; Novalab Limited; Mann Testing Laboratories; Wellington Environmental Consultants; and Zenon Environmental Laboratories. The laboratories have been given random numbers for the intercomparison. A comparison of the clean-up and analysis methods used by the various laboratories is shown below in Table 2.

TABLE 2: **Comparison of Clean-Up and Analysis Methods Used by Participating Laboratories.**

	MOE	ENVIRONMENT CANADA	ELI ECO	MANN	NOVALAB	WELLINGTON	ZENON
CLEAN-UP							
a. Extraction	Soxhlet - toluene	Soxhlet -toluene	Soxhlet -toluene	Soxhlet -toluene	Soxhlet -toluene	Soxhlet -toluene	Soxhlet -CH_2Cl_2
b. Column Clean-up	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina
c. Carbon Clean-up	none	none	Carbon on glass fibre	none	Carbopack C on Celite	none	none
ANALYSIS							
a. GC-MS	Finn TSQ70	Finn 4500	HP5970 MSD	Finn 4500	HP5970 MSD	VG 12000	Finn TSQ70
b. Final Volume (μL)	10	20	20	50	10	10	25
c. Injection Volume (μL)	2	2	2	2.5	2	2	1
d. Surrogates used ($^{13}C_{12}$-)	TCDD PCDD HxCDD HpCDD OCDD	TCDD PCDD HxCDD HpCDD OCDD TCDF	TCDD PCDD HxCDD HpCDD OCDD	TCDD OCDD	TCDD OCDD	TCDD PCDD HxCDD HpCDD OCDD	TCDD HxCDD OCDD
e. Peak Height or Area	area	area	area	area	area	height	area

Results from the exposed filter and PUF analysis and the spiked combined extract analysis are shown in Figures 3 and 4 respectively. For both analyses, there is considerable between-lab variability. When positives were detected, the number of isomers reported also varied from lab to lab. Some of the laboratories did not detect the spikes that had been added to the combined extract.

Results from the low level spiked blank are more consistent, with the exception of lab #3 not detecting the HxCDD spike. For the tetra-, hexa-, and octa- CDD congeners at respective spike levels of 12, 20, and 29 pg/μL, the average levels reported were; tetra: 11 ± 4; hexa: 16 ± 4 and; octa: 25 ± 10.

Reasonably consistent results were also obtained from analysis of the unknown standard mixture (Table 3). Some laboratories had trouble with certain congeners and overall standard deviations were larger for the higher chlorinated congeners.

TABLE 3: Analysis of an Unknown Standard Mixture (Concentrations in pg/µL).

LABORATORY	1	2	3	4	5	6	7	EXPECTED VALUES	AVERAGE
Congener									
TCDD	87	81	136	113	100	160	101	100	111 ± 28
PCDD	89	80	132	73	66	95	92	100	90 ± 21
HxCDD	180	170	189	89	130	170	151	160	154 ± 35
HpCDD	82	110	141	99	130	100	107	200	110 ± 20
OCDD	200	190	227	100	190	200	189	200	185 ± 40
TCDF	39	39	51	40	68	45	42	50	46 ± 11
PCDF	46	41	58	37	51	59	41	50	48 ± 9
HxCDF	71	72	102	61	100	98	72	80	82 ± 17
HpCDF	98	78	100	70	200	80	93	100	94 ± 57
OCDD	84	79	110	46	134	140	83	100	97 ± 33

Five of seven laboratories demonstrated capability for the analysis of dioxins and furans in ambient air, however, further analytical methodology development is required by all laboratories as evidenced by variable results from both the exposed sample and the spiked extract analysis.

CONCLUSIONS AND RECOMMENDATIONS

Levels of dioxins and furans in ambient air in Ontario are typical of those reported in the literature for other localities in North America. Analytical methodologies for ambient air samples need to be refined and the effect of sample to sample variation from collocated samplers should be investigated. A second inter-laboratory round robin with replicate samples is recommended.

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Hunt, G.T. and B.E. Maisel, 1989. Atmospheric PCDDs/PCDFs in wintertime in a northeastern U.S. urban coastal environment. Ninth Intl. Symp. on Chlorinated Dioxins and Related Compounds, Toronto, Ontario, September 1989.

Smith, R.M., et al, 1989. Continuing atmospheric studies of chlorinated dibenzofurans and dioxins in New York State. Ninth Intl. Symp. on Chlorinated Dioxins and Related Compounds, Toronto, Ontario, September 1989.

Tashiro, C., et al, 1989. Comparison of high volume sampling techniques for dioxins and furans in ambient air. Chemosphere 19 (1989) 1-6.

FIGURE 1: Dioxin and Furan Ambient Air Monitoring Locations.

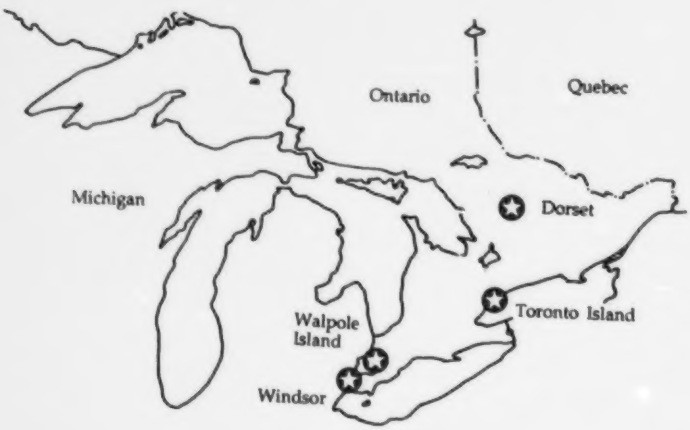

Ontario
Quebec
Michigan
Dorset
Toronto Island
Walpole Island
Windsor

FIGURE 2: Average Ambient Levels of Dioxins and Furans at Selected Sites in Ontario

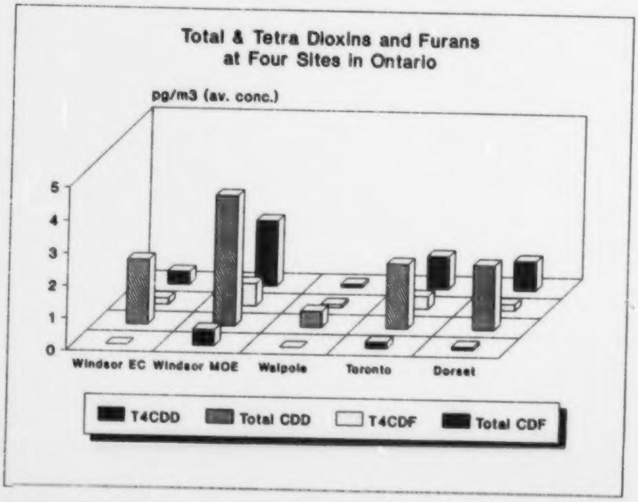
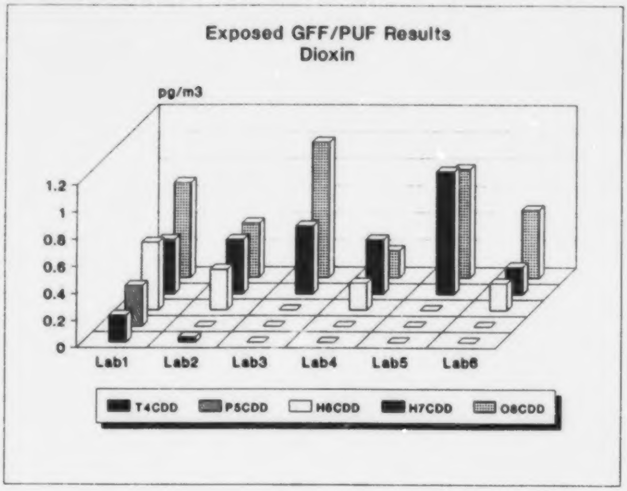


FIGURE 3: Round Robin Analytical Results: Exposed Filter and PUF Plug Analysis



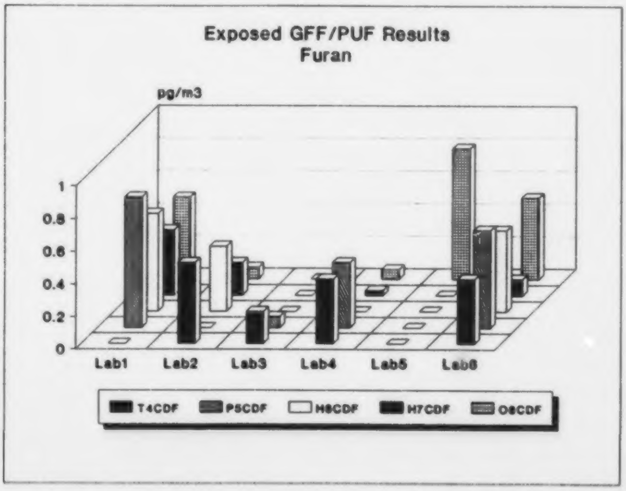
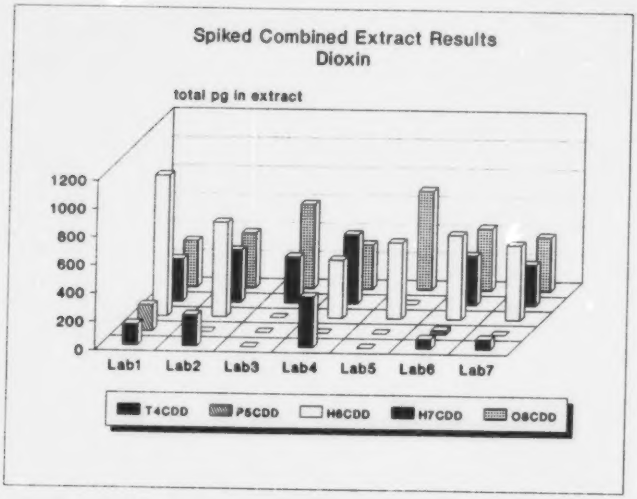
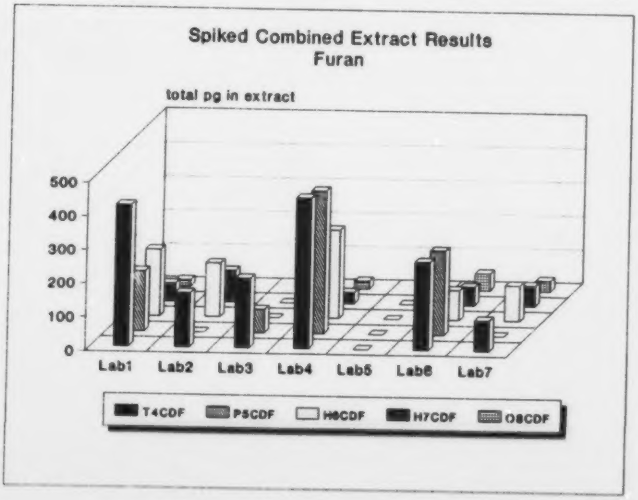


FIGURE 4: Round Robin Analytical Results: Spiked Combined Extract Analysis





A5

DEVELOPMENTS OF MONITORING METHODS FOR ODOROUS ORGANICS IN AMBIENT AIR

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INTRODUCTION

Odour nuisances have been reported in connection with facilities such as water treatment plants, kraft mills, rendering plants and oil refineries. The problem is that often the odour detection limit for the airborne compounds are lower than the current analytical detection limits: this is true particularly with sulfur containing compounds.

In the present study we are evaluating recent methods for the detection of four classes of compounds associated with odour complaints: aliphate amines; carbonyl compounds; short chain fatty acids; and sulfur containing compounds. With the exception of certain target sulfur compounds, the process of chemical derivatization followed by HPLC using either U.V. or fluorescent detection appears to be the best approach for obtaining detection limits in the low parts per billion range for most compounds under study.

METHODS

I AMINE ANALYSIS

SAMPLE PREPARATION[1]

Sep-PAK C_{18} cartridges were purchased from Waters Scientific, Mississauga and prepared as described below.

The Sep-PAK is initially washed with 5 mL methanol by attaching a syringe full of the solvent to the luer-look end of the cartridge and slowly passing methanol through. A second wash is then performed with a 3% (V/V) phosphoric acid solution in methanol using the same technique as above. The two ends of the Sep-PAK are then touched to a kimwipe, in order to remove any excess liquids.

The Sep-PAK is then placed in a vacuum manifold (Supelco Canada Inc.) and dried for one hour under reduced pressure and a nitrogen stream. Following this, the cartridge is placed directly under a stream of nitrogen for one half hour and a flow-rate of 80-100 mL/minute. The Sep-PAKS are placed in individually capped and labelled glass vials, and stored in a cool, dark, dry place for up to four weeks.

SAMPLING

The sampling apparatus is diagrammed in Figure 1. The flow rate is adjusted to be about 1 L/minute.

ANALYTICAL PROCESSING AND DERIVATIZATION

A stock basic methanol solution is prepared by weighing 0.166 g of KOH (BDH, Toronto) and dissolving it in 100 mL of distilled-in-glass methanol (Caledon, Georgetown). The derivatizing solution is made up by dissolving 0.200 g of 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl)(Aldrich) in 100 mL of the above basic methanol solution.

A 1 mL aliquot of NBD-Cl solution is then pipetted into 10 mL capped and labelled centrifuge tubes. Into these tubes the trapped amines are eluted by passing 5 mL of potassium hydroxide/methanol stock solution through the Sep-PAK cartridge. The tube is capped, vortexed for several seconds and incubated for a minimum of 24 hours at room temperature.

ANALYTICAL SYSTEM AND CONDITIONS

The analytical system and conditions for this evaluation are depicted in Figure 2. A Hewlett Packard model HP1090 HPLC system with the following components was used:

- gradient solvent delivery system
- variable volume injection system with autosampler
- variable wavelength, programmable fluorescence detector (some detectors are superior to others)
- integrator with a data system
- heated column compartment (optional)

The column necessary for the separation of the amines is Supelco's Supelcosil LC-18-S, a base deactivated, reversed phase octadecylsilane column. The column dimensions are: 25 cm x 46 mm with a 5 um particle size. The chromatographic conditions are listed below.

SOLVENT DELIVERY

Initial:	45% methanol, 55% water
6 minutes:	60% methanol, 40% water
Run time:	15 minutes
Flow rate:	1.5 mL/minute
Column Oven Temp:	40°C
Injection Volume:	20 uL

DETECTION

Lambda Excitation:	470 nm
Lambda Emission:	530 nm
Photomultiplier Tube Gain:	18 (maximum)
Response Time:	1000 msec

II ALDEHYDES AND KETONES ANALYSIS:

DNPH SOLUTION FOR COATING SEP-PAKS[2]

20.0 ml of saturated DNPH solution are added to 200 ml acetonitrile in a 1L volumetric flask with glass stopper. 1.0 ml conc H_3PO_4 is added, and solution shaken and made up to 1L volume with acetonitrile. The purity level of the solution is checked using HPLC.

COATING OF SEP-PAK CARTRIDGES

Each Sep-Pak is flushed with 10.0 ml acetonitrile using 10-ml syringe. An 7.0 ml aliquot of DNPH solution is dispensed through the Sep-Pak at a rate of 2.0 ml/min.

U.H.P. grade nitrogen is blown through the Sep-Paks via a DNPH guard column and drying manifold. (The use of paper towels should be avoided as these contain formaldehyde), at the rate of 50-100 ml/min for a few minutes (until no excess solvent droplets appear. Cartridges are then plugged at each end with luer lock male plugs and stored individually in glass culture tubes with either Teflon or polypropylene caps (Bakelite caps should be avoided as they are a source of formaldehyde)

PREPARATION OF DNPH-CARBONYL STANDARDS[3]

FORMALDEHYDE, ACETALDEHYDE, PROPIONALDEHYDE, ACETONE

A saturated solution of DNPH in 2N HCl is titrated with each of the above carbonyl compounds. The colored precipitate is washed with 2N HCl and water and air dried. Purity of derivative is determined by HPLC.

ACROLEIN, BUTYRALDEHYDE, BENZALDEHYDE, GLUTYRALDEHYDE[4], CYCLOHEXANONE (INT. STD).

The DNPH derivatives of these compounds are prepared by adding the carbonyl compound dropwise to an acidic solution of DNPH in dimethylsulfoxide (DMSO). The colored precipitate is filtered and washed with 2N HCl, and water. Purity is checked by HPLC. Individual stock solutions are prepared by dissolving 10 mg. of solid derivative in 100 ml of acetonitrile. A stock mixture of derivatives is similarly prepared.

SAMPLING PROCEDURE

The loaded Sep-Paks are attached via Tygon tubing, to a pumping system (Fig.1), which can be a Gillian pump or equivalent. Pumping rate should be adjusted to about 1 litre/minute. Flow rates are measured, using a 1 litre bubble meter, before and after sampling.

ANALYTICAL PROCESSING

Sep-Paks are eluted with 3.0 ml acetonitrile using a 5.0 ml syringe giving a final volume of 2.8 ml of eluent.

Samples are run on Hewlett Packard HPLC 1090A system using the following equipment and conditions (Figure 2).

Phenomenex 150 mm x 4.6 mm. ODS C_{18} column (or equivalent).
Hewlett Packard Diode array detector (or equivalent)
Solvent: 60% acetonitrile, 40% water.
Flow 1.0 ml/minute
Analytical wavelength 360 nm.
Oven temp. 40°C

GLUTYRALDEHYDE (1,5-PENTANEDIAL)

The following analytical conditions are used to chromatograph the DNPH derivative of glutyraldehyde.

Column: Zorbax CN column 4.6mm x 150mm
Mobile Phase
55% acetonitrile / 45% H_2O / 0.1% H_3PO_4

III

CARBOXYLIC ACID ANALYSIS

PREPARATION OF STANDARDS[6]

1-Pyrenyl diazomethane (PDAM). 50 mg of 1-pyrenecarboxaldehyde is suspended in 3 ml DMSO ; 0.3 ml of hydrazine monohydrate is added with sstirring, and the mixture stirred at 50-60°C for 3 hours. The yellow crytals of 1-pyrenecarboxaldehyde hydrazone are filtered and recrystallized from ethanol. Purity is checked by HPLC.

To 20 mg of the hydrazone suspended in 5 ml of diethyl ether and added 65 mg of activated manganese dioxide and the resulting mixture allowed to react in an ultrasonic water bath for 90 minutes. The manganese dioxide is filtered and the reddish-orange filtrate evaporated to dryness under nitrogen yielding red crystalline PDAM.

DERIVATIZATION OF FATTY ACIDS

To 2 mg of acid in 2.0 ml methanol are added 2.0 ml of 0.4% w/v solution of PDAM in ethyl acetate. The mixture is stirred for 2 hours at room temperature after which time a single peak is obtained on the chromatogram.

SEP-PAK PREPARATION

C18 cartridges are loaded with 1% sodium hydroxide in methanol. The cartridges are dried by flushing with pure nitrogen.

Recovery studies using standard fatty acids loaded onto prepared Sep-Paks, elution, and subsequent derivatization are still in progress.

ANALYTICAL PROCESSING

HP1090 system with fluorescent detection (lamda $_{ex}$ 230nm, lamda $_{em}$ 397nm)

Column: 15 cm Merck lichrosphere ODS (5u)
Solvent: 70% acetonitrile/30% water

STANDARD GAS GENERATION

Gas standards for individual target compounds are generated using a VICI Metronics dynacalibrator system, equipped with internal pump. Generated gas standards are diluted with zero air to give final concentrations in the low ppb range.

QA/QC

For samples a 20% QA/QC program should be implemented. This calls for 10% duplicate samples, 5% blanks and 5% spike recoveries.

RESULTS AND DISCUSSION

CHROMATOGRAPHY OF DERIVATIZED AMINES, CARBONYLS AND CARBOXYLIC ACIDS

Representative chromatograms of the target amine and carbonyl derivatives are shown in Figures 3 and 4. Glutyraldehyde-DNPH does not chromatograph well on ODS C18 column. Figure 5 shows the chromatogram for glutyaldehyde-DNPH using Zorbax CN column. The chromatogram for the pyrenyl esters of C_1 to C_6 carboxylic acids is shown in Figure 6.

Recoveries at three levels for target amines and carbonyl compounds are generally better than 85%. Preliminary studies on the carboxylic acids indicate similar recoveries.

Detection limits for target amine and carbonyl compounds are given in Tables 1 and 2. These detection limits correspond to a signal to noise ratio 5:1 and are determined by sequential dilution of stock standards. The ppbv values are based on an air sample of 150 litres for amines, and 100 litres for carbonyls.

CARBOXYLIC ACIDS AND SULFUR COMPOUNDS

At this stage it is clear that the derivatization of carboxylic acids using the fluorescent tag pyrenyl diazomethane (PDAM) provides a sensitive means of determining this class of compounds.

With the exception of butyric and isobutyric acid, which co-elute, good chromatographic separation is obtained for the remaining target compounds (Figure 6). Recoveries from the C18 Sep-Pak are good (>80%), and work in progress includes attempts at in-situ derivatization (on the Sep-Pak), as well as a comprehensive method validation.

The group of sulfur compounds owing to their reactivity, instability and low odour thresholds pose the greatest challenge. The thiols are amenable to derivatization using 7-Chloro-2, 1,3--benzoxadiazole-4-sulfonate (SBD-Cl)[6] with subsequent HPLC determination using fluorescent detection. Recent studies indicate that a structurally similar fluorescent tag may be used to derivatize disulfides[7]. We are presently investigating this in conjunction with a thermal desorption GC/MS method.

CONCLUSIONS

With the possible exception of sulfur compounds (methods for which are currently being evaluated) the process of concentrating airborne odorous compounds on to a suitable matrix, with either in-situ or post elution derivatization followed by HPLC, allows detection limits in the low ppbv range to be attained. Whilst the procedures are not new, the optimisation of variables (such as cartridge packing material, flow rates through the cartridge, pH of eluting solvent) combined with the development of a sampling train for field us for all four compound classes will provide the unique capability of narrowing the source of an odour problem to a compound group,with subsequent quantitation.

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[4] OSHA Analytical Laboratory, Salt Lake City, Method 64.

[5] Noriyuki Nimura, Tosaio Kinosaita; Anal. Chem., 1988, 60, 2067-2070.

[6] John L. Andrews, et. al.; Archives of Biochemistry and Biophysics, vol. 214, No. 1, March pp 386-396, 1982.

[7] Toshimasa Toyo'oka, Yukio Saito and Kazuhiro Imai; Analytica Chimica Acta, 205 (1988), 29-41.

Fig. 1 SAMPLING SYSTEM

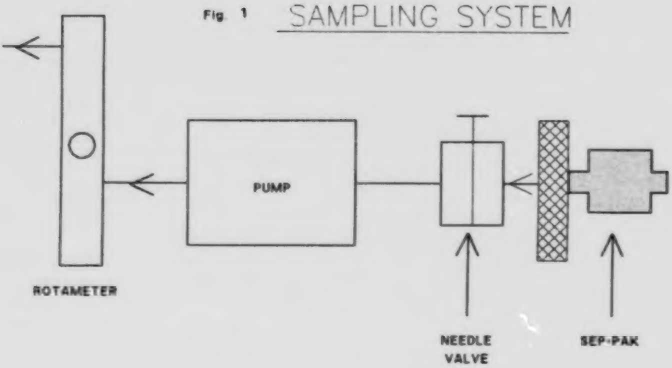

PUMP
ROTAMETER
NEEDLE VALVE
SEP-PAK

Fig. 2 HPLC SYSTEM

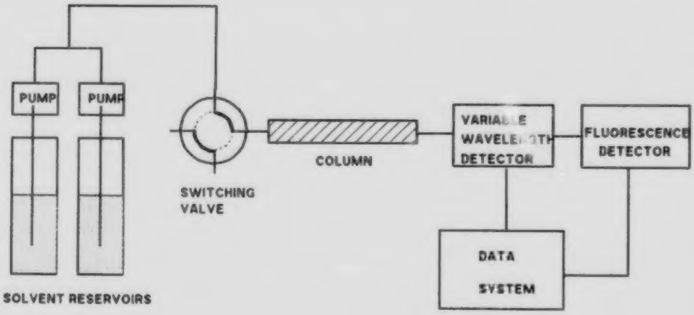

PUMP
PUMP
SOLVENT RESERVOIRS
SWITCHING VALVE
COLUMN
VARIABLE WAVELENGTH DETECTOR
FLUORESCENCE DETECTOR
DATA SYSTEM

FIGURE 3

Chromatogram of Amine-NBD Derivatives (Fluorescent Detection)

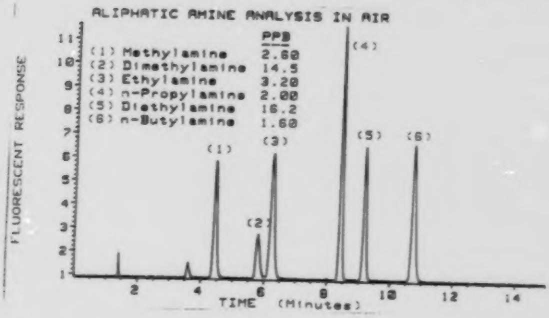
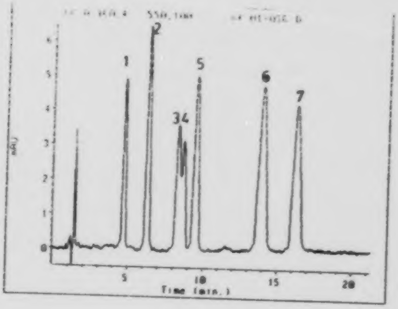


FIGURE 4

Chromatogram of Hydrazones (UV Detection)



		ng for 20 µl injn
1	FORMALDEHYDE	28·6
2	ACETALDEHYDE	54·0
3	ACROLEIN	72·0
4	ACETONE	34·0
5	PROPIONALDEHYDE	29·8
6	BUTYRALDEHYDE	68·0
7	BENZALDEHYDE	97·0.

ACETONITRILE/
WATER

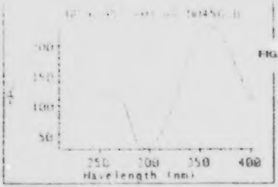
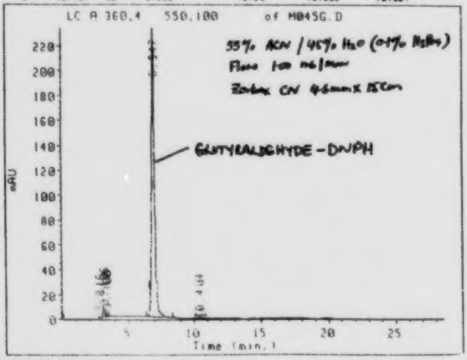


FIG. 5 GLUTYRALDEHYDE - DNPH

```
LC A 360.4   552,100       of M0456.D
DATA:M0456.D


Peak#  Ret Time  Type  Width          Area   Start Time   End Time
   1     2.816   BV    0.140          9.20        2.690      2.957
   2     3.106   VV    0.124         53.69        2.957      3.234
   3     3.300   VS    0.100         42.57        3.234      3.479
   4     6.947   BV    0.200       4244           6.349      8.365
   5    10.404   BB    0.238         10.29       10.002     10.861
```



55% ACN / 45% H₂O (0.1% H3PO4)
Flow 1.0 mL/min
Zorbax CN 4.6mm x 15cm

FIGURE 6

Chromatogram of C_2 to C_5 Pyrenyl Esters (Fluorescent Detection)

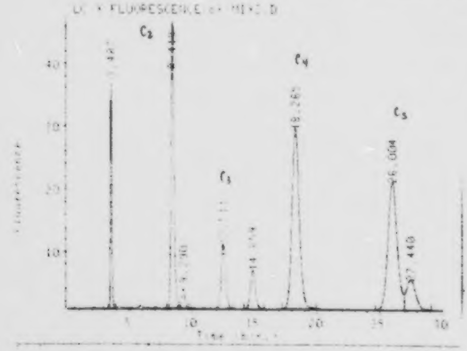


TABLE 1

METHOD DETECTION LIMITS FOR THE ANALYSIS OF ALIPHATIC AMINES IN AIR

	METHOD DETECTION LIMIT (ppb)	RSD (%)	DEGREE OF ERROR "D" (ppb)	LOWER LIMIT (ppb)	UPPER LIMIT (ppb)
METHYLAMINE	0.105	6.36	0.011	0.093	0.11[illegible]
DIMETHYLAMINE	0.043	4.99	0.001	0.041	0.044
ETHYLAMINE	0.063	10.5	0.006	0.056	0.069
n-PROPYLAMINE	0.039	15.3	0.005	0.034	0.045
DIETHYLAMINE	0.809	13.6	0.129	0.68	0.938
n-BUTYLAMINE	0.040	5.1	0.001	0.039	0.042

TABLE 2

Method Detection Limits
for
Carbonyl Compounds

	DETN LIMIT ng for 20 ul inj.	*DETN LIMIT ppbv	RSD %	DEGREE OF ERROR'D'	LOWER LIMIT ppbv	UPPER LIMIT ppbv
Formaldehyde	1.00	0.14	10.71	0.014	0.13	0.15
Acetaldehyde	0.90	0.13	18.45	0.022	0.11	0.15
Propionaldehyde	1.98	0.20	13.20	0.026	0.17	0.23
Butyraldehyde	2.30	0.25	24.80	0.058	0.19	0.31
Benzaldehyde	3.20	0.39	7.63	0.028	0.36	0.42
Glutyraldehyde	2.00	0.15	17.30	0.025	0.13	0.18
Acrolein	3.50	0.30	12.00	0.034	0.27	0.33
Acetone	3.00	0.25	16.40	0.039	0.21	0.29

* Based on a 100 litre air volume.

A6

AMBIENT AIR ANALYSIS WITH A THERMAL DESORPTION / GAS CHROMATOGRAPH / MATRIX ISOLATION / INFRARED SPECTROMETER SYSTEM

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INTRODUCTION

The detection and measurement of organic compounds in the ambient air by the staff at the Air Resources Branch of the Ontario Ministry of the Environment is presently accomplished by a gas chromatograph / mass selective detector system (GC/MSD). Organic airborne contaminants are collected on and thermally desorbed from a glass cartridge containing three layers of adsorbent materials, and then injected into the GC. The sample is split into three streams: two streams pass through capillary columns (of different polarity) to flame ionization detectors (FID); the other stream passes through a capillary column to the mass selective detector for generation of the mass spectra of the individual compounds. Compound identification is made by comparing the mass spectra to a library of known mass spectra, and by comparing the retention indices for the compounds (on the two columns connected to FIDs) to a user-generated library of known retention indices. Concentrations are determined by calibrating the GC system with standard injections and comparing the peak areas.

In some cases GC/MSD is not sufficient for complete characterization of the GC eluate due to the inability of the MSD to distinguish between certain isomers. Comparison of infrared spectra (IR) is a complementary technique to the MSD usage that can significantly improve the confidence and number of compound identifications in a sample. Until the last few years the IR method was relatively insensitive compared to mass spectrometry (MS); however the recent commercial introduction of a matrix isolation (MI) interface between a GC and a Fourier transform infrared (FT-IR) spectrometer has changed that relationship. The GC/MI/FT-IR system captures the compounds eluting from the GC column in an IR transparent matrix of solid argon at a temperature of 12K. The separated compounds can then be scanned with the FT-IR spectrometer for indefinite periods. Good quality MI/FT-IR spectra can be obtained for most organic compounds with less than 10 nanograms (10^{-9} gm), while the more polar molecules may be seen at levels of only 50 to 100 picograms (10^{-12} gm).

In addition to the equivalent sensitivity to MS, the MI/FT-IR spectra have very sharp features due to the extremely low temperature of the argon cage, the limited rotational motion of the trapped molecules, and the lack of intermolecular effects (argon:analyte ratio is approximately 1000:1). The simplified spectra with sharp features will usually ensure that different isomers can be easily distinguished.

The objective of this study was to evaluate thermal desorption of cartridges as an effective means of introducing air samples to the GC/MI/FT-IR system.

GENERAL DESCRIPTION OF THE METHOD

Ambient air samples were collected on three-layer adsorbent cartridges connected to Gilian samplers operating usually at a sample flow of 100 mL/min for 60 minutes, thereby giving a six litre sample. The adsorbents used were Carbotrap B, Carbotrap C and Spherocarb - each layer was about 2 cm long in the 7 mm id glass cartridge, separated and held in place by plugs of quartz wool. The loaded cartridge was loaded into a thermal desorption system (CRYOTHERM 8901) built by an instrument specialist at the Air Resources Branch. The cartridge was heated to 300 C for 7 minutes under a helium flow of 10 mL/min, thereby driving all contaminants through a Nafion dryer onto a short length (7 cm) of nickel capillary tubing (the "loop"), being cooled to a temperature of -180 C at one end and about -50 C at the other. The cold loop served to focus the contaminants into a small plug, which was then ballistically heated for 12 seconds under GC carrier gas purge (helium) and driven onto the head of the GC column for the start of the GC analysis. Figure 1 outlines the method.

The sample components passed through the GC column to a splitter which sent about 20 % to the FID and 80 % to an open-split interface, where the argon matrix gas was added to the eluate and then sent down the transfer line (240 C) to the slowly rotating cold disk (12 K, 10^{-5} torr). A solid argon track was formed on the disk surface with the eluted compounds embedded sequentially along its length according to their retention time on the GC column. The disk was then rotated 180 degrees to position the track in the optical path of the FT-IR spectrometer. The track was slowly stepped through the optical path, with the total IR absorbance measured at each step, to produce an IR chromatogram of the GC analysis. This IR chromatogram (PSIR) was used together with the FID chromatogram to decide where to collect IR spectra along the track. An example of both chromatograms is shown in Figure 2.

RESULTS AND DISCUSSION

The first test of the new desorption unit was to see how effective it was in desorbing cartridges spiked with a standard mixture of organic compounds. In comparison with standard injections at port #2 of aromatic and chlorinated organics, the peak areas and GC chromatograms were essentially identical. Redesorption of the same cartridge showed no residual peaks.

What else was trapped on the cartridge during sampling and then desorbed? Carbon dioxide and water were also seen in all samples in relatively large amounts. Fortunately they are both small molecules with fairly simple MI/IR spectra at 12K, so their characteristic absorption bands could often be subtracted from the sample spectra without problems.

Dryer

Several procedures were tried in order to minimize the water (important) and carbon dioxide effects on the system. The trapping of large amounts of water was expected, so the desorber was designed to include a Nafion dryer in-line between the cartridge and the cold "loop". Published results on Nafion dryer investigations also suggested that conditioning the dryer between samples by heating it up to 100 C, with purging gas, and cooling it down to ambient temperature, would improve the water removal effectiveness by a factor of 20.

RESULT: Based on visual comparison of the water droplets formed on the cartridge walls during the desorption step to the ice crystals formed on the cold disk during the GC analysis, the Nafion dryer is very effective in removing more than 90 % of the water.

GC oven temperature program

The standard procedure at the ARB lab was to start the GC analysis at an oven temperature of -60 C and ramp it up to 200 C at 10 /min. That temperature program in the present study led to a broad water peak covering the 3-10 minute period in the eluate, although only noticeable in the IR chromatogram and not in the FID response. A procedure that has met with some success was to start the GC analysis at oven temperature of +20 C, hold for 3.0 minutes, and then ramp at whatever rate desired.

RESULT: Holding the GC oven temperature at +20 C for the first 3.0 minutes focused both the carbon dioxide and the water into relatively narrow plugs that were mostly eluted by that time, allowing fairly clean spectra for compounds eluting after pentane (retention index = 500). Different conditions may be necessary to get clear results for the compounds eluting earlier.

Tenax GC

Another possibility that was investigated was to make a cartridge with Tenax GC as the adsorbent, and test the claim that it is hydrophobic, i.e. does not trap water.

RESULT: More than twice the usual amount of water was desorbed from the Tenax GC cartridge - visual observation only. The conclusion was that the present cartridge was satisfactory for now.

Quartz Wool

Ambient air samples spiked with standard injections were collected on cartridges packed only with quartz wool to determine if the water, carbon dioxide or the organics were being trapped on it to any extent, instead of completely on the three layers of adsorbents.

RESULT: The desorbed cartridges showed that nothing had been trapped on the quartz wool, making it entirely neutral in the adsorption/desorption process.

Ambient Samples

Ambient air samples were collected in the downtown Toronto area during July and August, in duplicate, by adjacent Gilian samplers operating at 100 mL/min for 60 minutes in most cases. One set of the cartridges was analyzed on the existing GC/MSD system at ARB. The other set was analyzed on the GC/MI/FT-IR system.

Attention was focused on 11 compounds (Table 1) from the target list of 22 compounds currently used at the ARB mobile support laboratory. MI/FT-IR spectra were obtained for each compound, baseline-corrected, then computer searched with a squared difference algorithm against a user-generated library of about 180 MI/FT-IR spectra and a commercial library of 5000 MI/FT-IR spectra (if necessary). Each spectral search with the small library took about 1.5 seconds, the large library about 1.5 minutes.

Identification

Identification by IR was considered accurate if a clear #1 choice was listed in the hit list or if all of the major spectral features were superimposable between the sample spectrum and the library spectrum. In all cases, if a sufficient amount of the compound was present, the #1 choice was clear or a quick visual comparison of the spectral features for the top 10 choices would determine the identity.

The operator of the GC/MSD system found a similar situation for the other sample set. A sufficient amount of material usually produced a #1 hit or it could be determined by quickly scanning visually through the top 10 choices. One of the uncertain areas, as expected, was distinguishing the xylene isomers.

Concentration

Although the primary strength of the GC/MI/FT-IR technique is unambiguous identification of the compounds, an initial attempt was made in this study to determine some concentrations based on the IR absorbance of one of the main spectral features for each compound - usually the largest one. Based on four replicate injections of a low concentration standard mixture, and assuming the Beer-Lambert to be true, the concentrations of the 11 target compounds were calculated for some of the ambient samples and compared with results from the GC/MSD system. In general the results were in quite good agreement and will be presented.

Other Results

There were a few samples taken in support of the mobile air monitoring units (MAMU) during their ambient air surveys in Ontario. Some of those findings will also be presented.

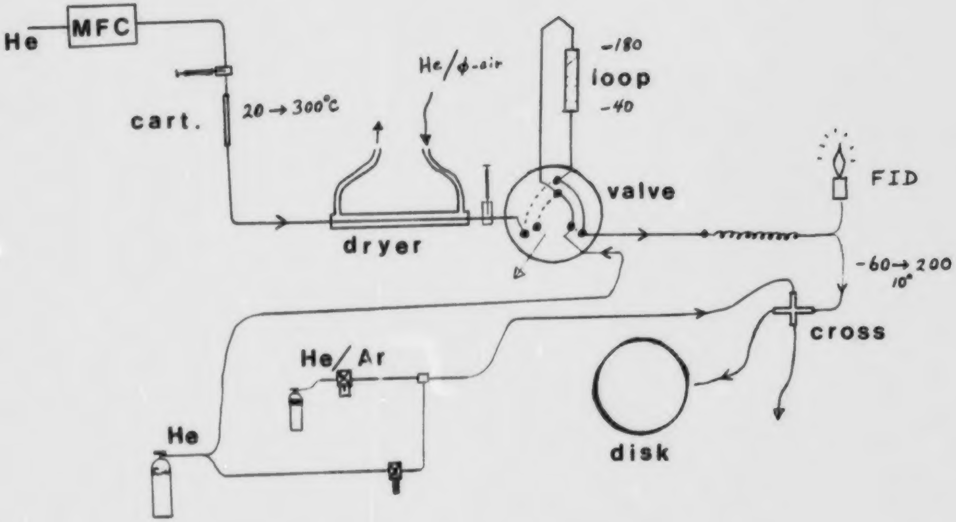
He
MFC
cart.
20 → 300°C
He/ϕ-air
dryer
-180
loop
-40
valve
FID
-60→ 200
10°
cross
He/ Ar
He
disk

FIGURE 1. Method Outline

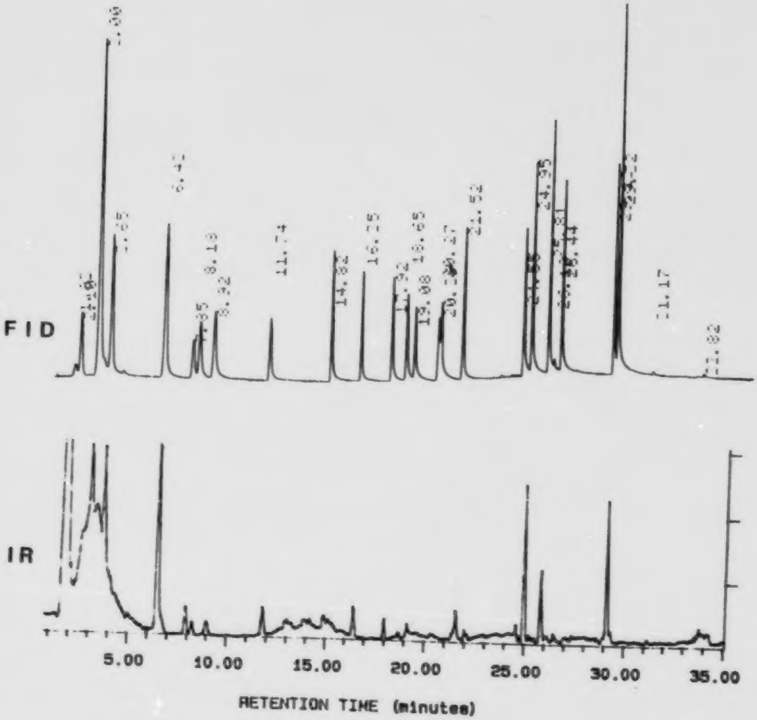

Figure 2 Chromatograms

TABLE 1

Target Compounds	Retention Time (min.)
1,1,1-trichloroethane	7.84
benzene	8.91
trichloroethene	11.74
toluene	14.82
tetrachloroethene	16.35
ethylbenzene	18.66
m,p-xylene	19.06
o-xylene	20.38
1,2,4-trimethylbenzene	24.55
1,2,4-trichlorobenzene	29.13
naphthalene	29.34

Note 1. Retention times based on a GC oven temperature program of: hold at +20C for 10 min., 10 deg/min up to 73C, hold for 5 min, and 10 deg/min up to 200C

A7

ATMOSPHERIC MEASUREMENTS OF NATURAL HYDROCARBONS USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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BACKGROUND

Concerted research efforts are being made to better understand atmospheric processes relevant to the oxidant/acid rain problem in Canada (1). In particular, a major research program called EMEFS (i.e. Eulerian Model Evaluation Field Study) was launched in June of 1988, to provide data for evaluating the Eulerian long-range transport oxidant/acid deposition models (ADOM and RADM) currently under development in Canada and the United States. Included as part of this study is a Canadian Atmospheric Chemistry Experiment (CACE) designed as intensive chemistry measurement programs to provide data for number of key species in the oxidant/acid rain problem which will not be routinely monitored during the core program of the EMEFS. One of the CACE projects addresses specifically the relative importance of NO_x and hydrocarbon, and natural vs. anthropogenic hydrocarbons in controlling atmospheric oxidants. The present program deals with measurements of natural hydrocarbons particularly relevant to this project.

Role of Natural Hydrocarbons as Oxidant Precursor: It is now well-recognized that the potential for photochemical production of ozone (O_3) and other oxidants from the oxidation of natural and anthropogenic hydrocarbons (HC), with oxides of nitrogen (NO_x) acting as catalyst, is enormous (2). In urban atmospheres, anthropogenic emissions of HC and NO_x clearly lead to high oxidant concentrations. Also, frequent occurrence of high O_3 concentrations (≥80 ppb) at rural sites in southern Canada has been of great concern because of its impacts on crop yield losses and its role in forest declines (1). Various modelling studies suggest production of high O_3 concentrations if sufficient concentrations of HC are present together with NO_x. However, ambient HC concentrations and HC/NO_x ratios at both urban and rural sites in Canada are still highly uncertain.

The total emission rate of natural HC such as isoprene and terpenes, has been estimated to be as large or larger than that of anthropogenic HC on a regional scale. In the U.S., 63% of the total nonmethane hydrocarbon (NMHC) emissions are of natural and 37% of anthropogenic origin (3). A similar situation also exists in Canada (4). Natural emissions are strongly influenced by temperature and are most dominant in the summer. Also, since natural NMHCs are more reactive than most of the anthropogenic NMHCs, a large impact of the natural NMHCs on the photochemistry of the rural atmosphere can be expected. Although the mixing ratios of these compounds are expected to be often below 1 ppb, the importance of these compounds in atmospheric chemistry is magnified by their high reactivity and by the multitude of reactions in which they participate in the atmosphere. They readily undergo reactions with the key oxidizing species such as HO, O_3, and NO_3. Initial products of these reactions include carbonyls (i.e. aldehydes and ketones) and oxygenated organic radicals. These species can, in turn, oxidize NO to NO_2 and subsequently lead to O_3 production after the photodissociation of NO_2.

A recent case study at a rural site in Pennsylvania by Trainer et al. (5) show that the oxidation of anthropogenic NO_x in the presence of naturally emitted isoprene, at concentrations observed at this rural site, can lead to high O_3 concentrations (80 ppb). Furthermore, a recent modelling study of urban O_3 concentrations in Atlanta, Georgia, by Chameides et al. (6) indicates that natural NMHCs are a significant controlling factor. Also, Altshuller (7) recently reported an updated assessment of the oxidant forming potential of nonmethane organic compound to nitrogen oxide ratios and organic composition in North American cities and rural areas.

Measurements of Natural Hydrocarbons in Ambient Air: Among numerous known natural hydrocarbons, isoprene and mono-terpenes emitted from deciduous and coniferous trees, respectively, are of particular interest to an assessment of rural ozone in a Canadian setting, e.g. the Ministry's Dorset and other forested sites (3,8). Due to their high reactivity coupled with their emission rates which are very sensitive to temperature, sun light and humidity, their atmospheric distributions can exhibit a large magnitude of spatial and temporal variability. Furthermore, the pattern of hydrocarbons in rural atmosphere is quite complex due to contributions from anthropogenic sources (3). Over the years, gas chromatography in combination with preconcentration methods has evolved as the most suitable method for atmospheric measurements of hydrocarbons including these natural hydrocarbons (8,9). However, there is still a lack of well-established techniques which allow measurements of a wide range of these labile organic compounds on a routine basis with adequate precision, sensitivity and selectivity. An important component of this proposal is a critical evaluation and improvement of existing sample collection and handling techniques for GC/MS-based identification and quantification of these trace gases.

A relatively large sample volume of typically 1 dm^3 (STP) is necessary to achieve the desired lower limits of detection of some ppt for these hydrocarbons. Consequently, some preconcentration procedure is required in order to reduce the sample size sufficiently to allow injection and separation in a gas chromatographic system. One rather simple, convenient way of achieving this step is to collect air samples using adsorptive sampling on solid sorbents such as Tenax, XAD-resins, Carbosieve, etc., followed by thermal desorption of the concentrated samples. This approach has been used for measurements of mono-terpenes (12,13). However, the sampling efficiency of these sorbents for hydrocarbons of high volatility is often not very good. Furthermore, the formation of artefacts during sampling, storage or sample desorption has been reported (8). In any case, the sampling efficiency and sample integrity must be tested and ensured for these sampling and handling procedures.

Another commonly used method is to collect whole air samples in stainless steel flasks by pressurizing the samples by means of either metal-bellows pumps or cryogenic collection in order to condense large volumes of air into a small sample container (9). A separation of nitrogen and oxygen from the low and medium molecular weight hydrocarbons can be achieved by adsorbing the trace gases on some solid sorbent such as porous silica, alumina, graphite or porous glass beads at subambient temperatures. For instance, a small stainless steel precolumn (15 cm length, 2 mm i.d.) packed with porous beads (0.35 micrometer) at about 80 K has been reported to adsorb all hydrocarbons except methane. This type of preconcentration column has been shown to cause neither detectable blank values nor any measurable memory effects from one sample to the next (3,9). The major practical problems of flask sampling are high costs of containers and logistics for sample collection and transporting them. Also, the stability of the trace gases in the sample container must be tested occasionally. Namely, if the ambient ozone is retained in the container, both isoprene and mono-terpenes can be decomposed rapidly. Furthermore, the presence of a substantial amount of water in the sample injected onto the separation column prohibits the use of any small bore capillary column operated at subambient temperatures. The use of a drying agent such as $Mg(ClO_4)_2$ or K_2CO_3 for removing the water can, in some instances, cause severe changes in sample compositions (10).

Scope of the Project: In conjunction with the planned field measurements, methodology development and testing required for measurements of hydrocarbons are being carried out concomitantly. Notable among these research activities are design and construction of an efficient heated vacuum facility for cleaning air sampling flasks, development and testing of cryogenic sample preconcentration units, and comparative evaluation of several selected GC columns. In our laboratory, the cryogenic flask sampling and the preconcentration method described above have been in use for measurements of low molecular weight halocarbons in non-urban atmosphere, and an initial feasibility study for analysis of natural hydrocarbons has been carried out using this system. A new preconcentration - injection system patterned after that developed by Rudolph et al. (9) has been designed prior to the initiation of this project, and further development of this unit is intended to serve as a reference method for comparison with other sample handling methods such as thermal adsorption-desorption methods. An overall performance evaluation for hydrocarbon analysis is based both on systematic examination of various operating parameters and on inter-laboratory comparison of results obtained from field measurements with other groups. Furthermore, whenever possible, comparisons of results from the analysis of air samples collected in stainless steel flasks with those of direct on-site measurements are intended throughout this project to examine sample integrity.

METHODOLOGY DEVELOPMENT AND TESTING

Heated Vacuum Facility for Cleaning Air Sampling Flasks: Field measurements of hydrocarbons using flask sampling require a large number of flasks and a suitable flask cleaning facility. To employ a cleaning procedure established by Rudolph et al. (9), a vacuum-oven facility was designed and built in-house which consists of an all stainless steel vacuum manifold with eight flask-connection ports, an oven housing (3'x4'x4') operated up to 100 ^{o}C, liquid N_2 trap, high speed turbo pump and mechanical pump. After connecting flasks the vacuum manifold is lowered into the oven pneumatically, and the heating and pumping operations are automatically controlled. Using this facility up to eight flasks could be evacuated simultaneously down to 1×10^{-6} mmHg in 30 min. During the EMEFS Summer-88 program over five hundred electropolished stainless steel flasks (3 litre volume) obtained from Oregon Graduate Center were cleaned using this facility.

Cryogenic Sample Preconcentration Units: Altogether three all-stainless steel vacuum cryogenic preconcentration units have been designed and assembled. Shown in Figure 1 is a schematic diagram of such a unit. One of the units is encased in a housing heated up to 90 C. This provision was found necessary to reliably handle heavy hydrocarbons such as aromatics and mono-terpenes. The second unit operated at near room temperature is dedicated to analysis of C_2 hydrocarbons only. The third and the most improved preconcentration - injection unit which has automated valve control and adjustable cryogenic temperature control is under development for use as a reference sample handling device for the GC/MS instrument. Performance of its major components proved satisfactory and the electro-mechanical control unit for automatic control of the entire operation is being tested.

GC/FID and GC/MSD Instrumentation: Several GC columns including packed (10 ft. Porapak N, 80/100 mesh), narrow bore capillary columns (30 & 60 meters) have been tested for the analysis of hydrocarbons in the C_2 to C_{10} range using sub-ambient temperature (-60 ^{o}C) operation programmed to 200 ^{o}C. The in-house built cryofocusing units have been installed to achieve optimum column resolution. Also, a 50 meter plot column (Al_2O_3) is being tested for C_2 - C_6 hydrocarbons. Since a single column is not capable of resolving the full range of C_2 - C_{10} hydrocarbons, two different columns and dedicated GC instruments are being employed for the analysis of light and heavy fractions. Figure 2 illustrates the light hydrocarbon portion of typical chromatograms recorded air samples collected at the Ministry's Dorset site. In addition, to obtain unique identification of GC peaks a new GC/MSD Quadruple (Hewlett Packard) has been installed and tested using a capillary column and various neat samples including mono-terpenes (cf. Figure 3).

FIELD MEASUREMENTS

EMEFS Summer-88 Program: During July 20 - August 31, 1988, over 400 flask samples were collected altogether at two ground sites (Dorset and Egbert, 3 samples per day) and aloft with two aircraft flying over these sites. Extensive measurements of hydrocarbons were carried out collaboratively by five groups (AES, Concord, OME, Hydro, C&P and York U.). In addition to sample analyses, the York group was in charge of bookkeeping, shipping, cartridge loading (for OME analysis), and flask cleaning. Also, during the month of August 1988, the York group collected in total 40 samples at the Borden site in and above the tree canopy to better characterize biogenic hydrocarbons. These summer activities were followed by intercomparison of absolute standards and blended mixtures, testing of sample stability in the flasks, and leak testing of flask valves. Data analysis and interpretation including computer modelling are underway.

Although the hydrocarbon data from the EMEFS Summer-88 program have not yet been fully analyzed, some notable results concerning natural hydrocarbons can be summarized as follows.

(1) Isoprene was detected in the majority of air samples collected at the ground sites during day hours, and its concentrations were the highest under stagnant high pressure system, e.g. in the early part of August. For instance, over the tree canopy at the Borden site its concentrations were measured to be as high as 6 ppbV (cf. Figure 4).

(2) Atmospheric samples containing C_2 - C_5 including isoprene appear to be stable in the stainless steel flasks during storage over a period of one week.

(3) Our isoprene data are highly consistent with those obtained by the Concord Scientific group (cf. Figure 5).

Based on an analysis of hydroxyl (HO) radical reactivity of various light hydrocarbons (C_2 - C_5) observed at the Ministry's Dorset site during the episodic conditions, isoprene has been shown to play a significant (often dominant) role over the anthropogenic hydrocarbons in local chemistry leading to the oxidant production.

OME Dorset Summer-89 Program: On-site measurements of hydrocarbons, particularly isoprene, using a mobile laboratory have been conducted in collaboration with AES and Hydro groups in attempts to obtain a representative set of data on diurnal and vertical distributions during the period of episodic conditions rather than taking three samples a day as done in the previous year. The on-site measurements also provided an opportunity to compare and test direct vs. flask sampling methods. Figure 4 illustrates a 24 hour data on isoprene and other hydrocarbons recorded at the ground level during sunny stagnant conditions. Isoprene is seen in this figure to rapidly reach a steady level at about 2 ppbV after sunrise and to gradually decrease at nighttime. These observations appear to be consistent with the fact that emission of isoprene from deciduous trees occurs primarily during day hours under hot, humid conditions (3). Note that the Ministry's site at Dorset is surrounded mainly by deciduous rather than coniferous trees, and thus, that the dominant biogenic hydrocarbon is expected to be isoprene and not mono-terpenes. Suitability of these data for making a detailed 1-D modelling study is being examined.

CONCLUSION

Various tests for quantitative analysis of light hydrocarbons up to C_5 (e.g. isoprene) by GC method in combination with stainless steel flask sampling and cryo-preconcentration method have thus far revealed no inherent technical problems. On the other hand, there remain a large number of sample integrity tests to be performed for heavy hydrocarbons, particularly monoterpenes and aromatics, in order to establish a fully validated sample handling method. Future work will focus on such methodology development and testing in conjunction with the planned field studies.

ACKNOWLEDGEMENTS

We are grateful to the Air Resources Branch of the Ontario Ministry of the Environment, the Atmospheric Environment Service of Environment Canada, and the Natural Sciences and Engineering Research Council for financial support of this work. We wish to thank all those who made valuable technical contributions, particularly our research group (J. Baumann, B. Kieser, G. Kiesel, E. Komor, J. Lai, and H. Malle).

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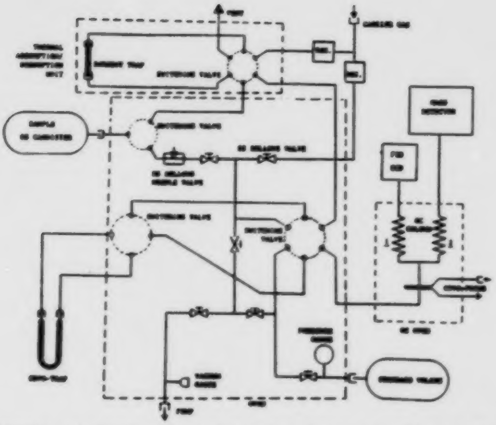


Fig.1: Schematic of Sample Preconcentration System for GC and GC/MS Analysis

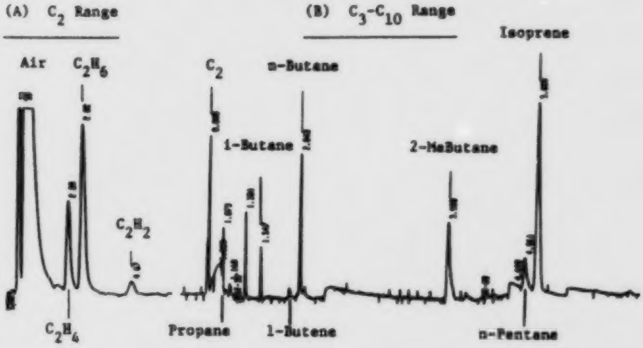
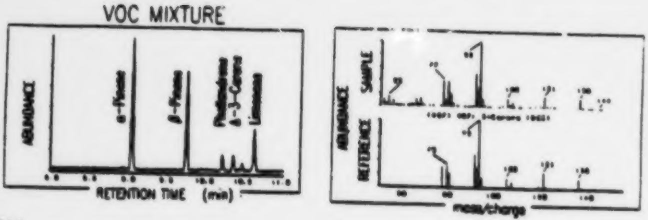


Fig. 2: Hydrocarbon Chromatograms of Air Samples (OHE Dorset Site)



(A)

(B)

Fig.3: GC/MSD Analysis of mon-terpenes: (A) Chromatogram using MSD in scan mode; (B) Sample vs. Library Reference Mass Spectra

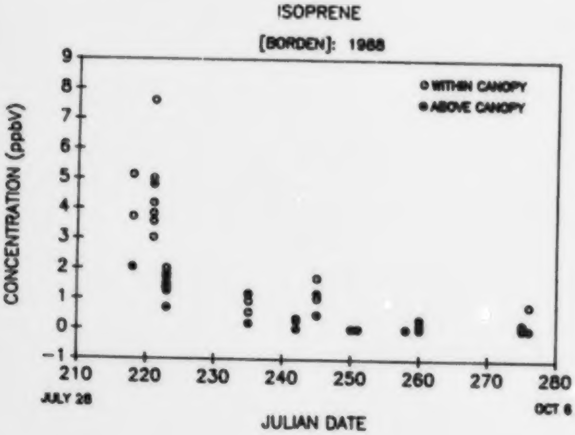


Fig.4: Concentrations of isoprene above and below tree canopy at Borden

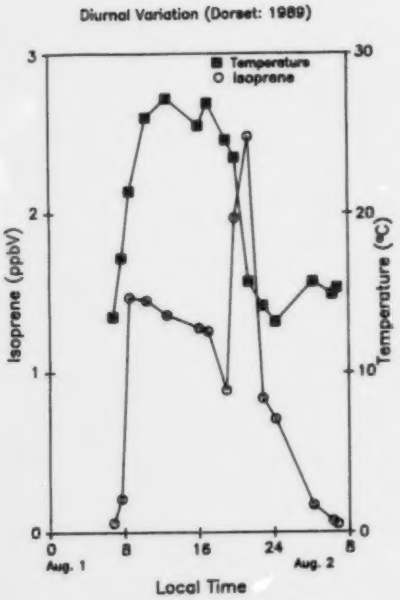


Fig.6: Diurnal variation of isoprene vs. temperature at Dorset

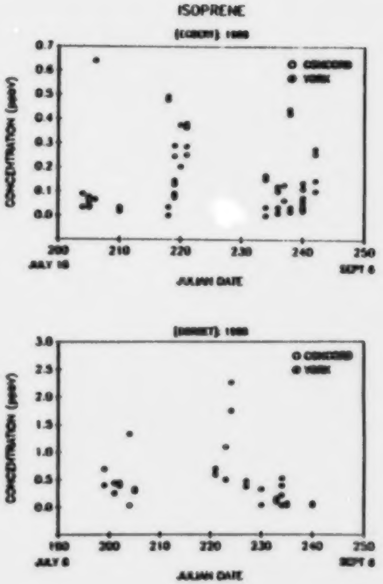


Fig.5: Isoprene data from Dorset and Egbert

A8

Multiple Option Approach to the Risk Assessment For Mixtures: Experience With Polycyclic Aromatic Hydrocarbons (PAH)

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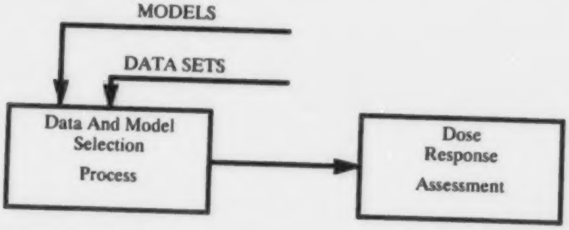
1 INTRODUCTION

1.1 Background

Our group is involved in the preparation of a report on the risk to man and other biota from a multimedia exposure to PAH-containing complex mixtures. The approach described below was developed to assist our group in this endeavor. The database for PAH is extensive and many different approaches to risk assessment could be attempted. We have opted for the development of a formal process to guide us through the selection of the best alternative(s). It is useful to visualize this process as a "front end" to the risk assessment process, because the process helps in the selection of the most suitable approaches to risk assessment (models) and the data these models use (See fig.1 and sections 1.2 and 1.3).

Fig. 1: **Proposed data and model selection process serves as a front end to the risk assessment process.**



1.2 Selection of Models

Over the years, a number of risk assessment models have been applied to PAH and PAH-containing complex mixtures. The sections below provide a description of a few of them.

My thanks to B. Thorpe and Drs. B. Birmingham and J. Lewtas for their comments and support throughout the development of this approach.

This work was performed as a part of development of multimedia standards for PAH - containing mixtures by the Ontario Ministry of the Environment, Hazardous Contaminants Coordination Branch.

1.2.1 Benzo[a]pyrene (B[a]P) Equivalents Model

Thorslund and Charnley [1] proposed to convert the potency of individual PAH in a complex mixture into B[a]P equivalents. The concentration of PAH in a complex mixture is then expressed in terms of the equivalents of B[a]P. The potency of such a mixture is assumed to be equal to that of B[a]P of the same concentration. The authors refer to this approach as a "comparative potency approach", a name which is unfortunately the same as that Albert et al.,1983 [2] have proposed for a different model. Our Ministry used a model similar to that of Thorslund and Charnley for dioxins and dibenzofurans, using 2,3,7,8-T_4CDD as the "standard" [3].

To apply the B[a]P Equivalents model to a given complex mixture, concentration data for each PAH within the mixture must be available.

1.2.2 B[a]P Equipotency Model

For risk assessment purposes, it is assumed that all PAH in complex mixtures are equal in potency to benzo[a]pyrene. This approach has been proposed by US EPA [4] and applied to complex mixtures [5].

To apply the B[a]P Equipotency Model to a given complex mixture, total PAH or Polycyclic Organic Matter (POM) concentration data is required.

1.2.3 B[a]P Proportional Potency Model

For risk assessment purposes, it is assumed that the potency of a PAH - containing mixture is directly proportional to its benzo[a]pyrene content. Pike and Henderson [6] suggested that 15 ng/m^3 of B[a]P be considered as equivalent in its human lung risk to a single cigarette. WHO used the B[a]P Proportional Potency Model for their Drinking Water Guidelines [7] and Air Quality Guidelines for Europe [8].

Application of the B[a]P Proportional Potency Model requires that the concentration of B[a]P in a complex mixture be known.

1.2.4 Comparative Potency Model

For risk assessment purposes, it is assumed that for all PAH-containing complex mixtures, the ratio of the potency of a mixture in man and the potency of that mixture in an appropriate experimental test is a constant C (see equation 1.)

Equation 1.

$$C = \frac{(humanrisk(mixt.1))}{(exper.potency(mixt.1))} = \frac{(humanrisk(mixt.2))}{(exper.potency(mixt.2))}$$

From this equation, the human risk for an unknown complex mixture (mixture 2) can easily be derived by the rearrangement of equation 1 (see equation 2).

Equation 2.

$$humanrisk(mixt.2) = C * exper.potency(mixt.2)$$

Use of the Comparative Potency Model requires knowledge of the concentration of the complex mixture within a given medium (for example, the amount of benzene-soluble fraction extracted from coke oven emissions).

It is possible to use other models in risk assessment of PAH-containing mixtures and some will be discussed later in this document. Each of these models has its advantages and disadvantages. It is difficult to identify the most promising one without assessing the data sets on which these models rely.

1.3 Selection of Data

Many regulatory agencies use a risk assessment process to estimate human risk of non-treshhold toxicants such as carcinogens [9],[10]. Despite the popularity of this process, the estimates derived from it are not always reliable. Most efforts have focused on improving the reliability of the extrapolation from experimental animal studies to man [11],[12],[13],[14],[15],[16],[17],[18]. The reliability of the risk estimate is dependent not only on the sophistication of these extrapolations, but also on the quality and general suitability of the data used for the risk assessment.

In order to estimate risk, a collection of diverse data is required, referred to here as a data set. Some data sets require relatively little extrapolation in order to estimate human risk. We will refer to such data as most "appropriate". For example US EPA [19] recommends the use of human data in preference to animal data (see table 1.), presumably because human data require fewer extrapolations in order to be applicable for establishing risk to general population.

Table 1. Appropriateness of data
(In the order of descending "Appropriateness")

- Human data in preference to animal data
- Data from the species responding most like human
- Other species

(USEPA, 1986 Guidelines for the Carcinogen Risk Assessment)

The most appropriate type of data may not be always available or data which is available may be of poor quality. For example, the data set may be incomplete or derived from studies with design flaws or shortcomings in data analysis. Therefore, it is necessary to consider both the quality and the appropriateness of the data, when selecting data sets for risk assessment. The US EPA addressed the issue of data selection in its guidelines for mixtures [20]. It recommends the selection of the most appropriate data set, for which the data are of adequate quality. This approach places a relatively heavy emphasis on the appropriateness of the data, and less on the quality of the data. This approach may often be reasonable, considering that the errors resulting from extrapolation from less appropriate data are likely to be larger than the errors which arise from using data of low quality. There are however, alternatives to this approach. The most robust risk estimate will be the one based on data sets where there is an optimal balance between the appropriateness and quality of data. The appropriateness and quality evaluations are performed for each data set and the best candidate(s) are selected.

1.4 Relation between the models and data

While sections 1.2 and 1.3 describe the selection of risk assessment models and their attendant data sets separately, the models and the data sets are , in fact, closely related since selection of one directs the selection of the other. Consequently the models and their respective data sets must be evaluated together. In this report, we describe a formal process for evaluation of the models and data sets, the goal of which is to identify the models and data sets which are likely to provide the most reliable estimate of human risk.

1.5 Rationale for the proposed approach

There were three reasons for developing a formal process for selecting models and data sets for subsequent risk assessment:

a) The shear volume of potentially relevant literature makes it impractical to give equal attention to the entire PAH literature. A formal approach helps identify the most relevant information for risk assessment. The selected areas can then be reviewed in greater depth.

b) Throughout the risk assessment process, value judgements are made frequently and unavoidably. Our regulatory process is open to public scrutiny, and it is therefore necessary to make value judgements explicit. Our formal approach has a built-in mechanism to make most of the value judgements explicit and the rationale for these value judgements is clearly spelled out.

c) It is difficult to decide on the most appropriate model until the analysis of the supporting data can be performed. Our process delays a commitment to a specific model until the quality of the available data for all of the models is evaluated.

2 DESCRIPTION OF THE PROPOSED APPROACH

2.1 General Approach

The general approach we propose and the various stages involved are outlined below.

Step 1: Several strategies (models) for assessing risk are predefined. Examples of such models are given in section 1.2.

Step 2: The assumptions for each model are defined. For example, one of the assumptions for 1.2.1 described in section 1.2.1 states that the risks from the exposure to the ingredients of the mixture are additive.

The assumptions are often shared by different models, but each model is based by unique set of assumptions.

Step 3: Each assumption is evaluated and the validity of each is determined. The validity of the assumption is expressed as a numerical rank.

It is presumed, that the robustness of a model is a function of the validity of the assumptions upon which the model is based. For many assumptions, the answer is not a simple "valid" or "not valid". The confidence in the available information may vary based on quality, quantity and general agreement within the literature. The assumption may also be valid under some, but not other conditions (limits). The assumption may also not be strictly speaking valid, but it may approximate reality closely enough to be treated as valid.

Step 4: The robustness of each of the models is ranked.

The ranking takes into account the validity of the assumptions on which the models are based and the dependence of the models on individual assumptions.

Step 5: Two or more of the highest ranked models may be used for the evaluation of risk. The results from these risk assessments can be compared and the best estimate of risk can be recommended for the development of a standard or guideline.

2.2 Application of the approach to PAH and PAH-containing mixtures

2.2.1 Description of the models

In section 1.2 we have described the different models used by different regulatory agencies and researchers to estimate the risk to man from exposure to PAH. In this section, We will present the approaches we are considering for the dose-response assessment of PAH.

2.2.1.1 Individual Compound Model

The risk associated with any given mixture is then estimated from the sum of the individual risks contributed by each PAH in the mixture. In order to use the Individual Compound Model, a quantitative chemical analysis is required for each mixture or medium for which a quantitative health risk is to be established.

Since human data is not available for individual PAH, the activity of each PAH is determined form experimental long and short-term data.

2.2.1.2 Grouped Compound Model

Individual PAH are grouped into a few classes, which reflect similarities in structure, relative activity and assumed similarities in the mechanisms in action. Each group is "assigned" a potency. Every compound within a group is assumed to have the same potency. The potencies of the groups, rather then individual PAH are summed in order to estimate the activity of the mixture as a whole.

2.2.1.3 Lumped Compound Model

All PAH-containing mixtures, such as coke oven emissions, are "assigned" the same potency. The risk estimate for a particular mixture is based on some measure of its concentration in a given medium and the assigned potency. In essence, this approach treats all mixtures as "essentially same" and consisting of a "single compound".

2.2.1.4 Models based on equivalents of single compound or mixture

2.2.1.4.1 B[a]P equivalents.

The potency of each individual PAH is expressed in terms of equivalents of a "classical" PAH (such as B[a]P). In order to estimate the activity of a particular mixture, the quantities of each PAH in the mixture is determined, translated into the number of B[a]P equivalents and summed up. This approach is numerically equivalent to the approach outlined in section 2.2.1.1. This approach is advocated by Thorslund and Charnley, 1988 [1].

2.2.1.4.2 Coke oven emission or Cigarette smoke condensate equivalents

The activity of each mixture is converted into the equivalents of a "standard" mixture with a known risk (Coke oven emissions or cigarette smoke condensate could be used as standards)

2.2.1.5 Source Mixtures Model

Unit risk is estimated for each type of source (coke oven emissions, diesel emissions etc.). The relative contribution of risk of each of these Source Mixtures to the overall mixture at the receptor level (an area where target is exposed, called Receptor Mixture) is estimated. The expected carcinogenic risk of the Receptor Mixture is calculated by summing the risks attributable to each of the sources (see equation 3:

Equation 3.

$$TCR = CM1 + CM2 + CM3 + \ldots CMn = (CS1 * QS1) + (CS2 * QS2) + \ldots.$$

where:

TCR = total carcinogenic risk of all Receptor Mixtures derived from all media (air, ambient water, drinking water...).
CM1, CM2 = total carcinogenic risk of all Receptor Mixtures derived from a specific medium.
CMn = total carcinogenic risk of all Receptor Mixtures derived from nth medium.
CS1, CS2 = carcinogenic activity of a particular type of PAH source per unit quantity
QS1, QS2 = quantity of a particular type of PAH source

2.2.1.6 The Monitoring Model

The carcinogenicity of an environmental mixture containing PAH is estimated from the genotoxicity of this mixture in short-term assays.

2.2.1.7 The "Blending Model"

The Blending approach **simulates** blending of the mixtures for which the risk and the composition is known (known mixtures) to reconstitute a mixture with the same composition as the mixture for which the risk is to be estimated (unknown mixture). The risk associated with the unknown mixture is estimated by summing the risk contributed by each of the known mixtures. In some cases, it may become necessary to add some individual PAH to the blend in addition to the known mixtures. **It should be stressed however, that it is not assumed that the unknown mixture was actually formed from the known mixtures as calculated in the Blending approach.**

2.2.2 Identification of the assumptions

Each of the models described above is based on a series of assumptions. The most robust model is the model based on the most robust set of assumptions. None of the models requires all of the assumptions listed in table 2. Each model is based on a different mix of assumptions from that table.

It is not expected that any of the models will satisfy all of the assumptions completely.

Collectively the assumptions required for any given model indicate how appropriate (see section 1.3) the data set is for that model. In an ideal model, where the risk could be determined directly on the population of interest, few assumptions would be required and the data set would therefore contain the most appropriate data set.

Table 2. List of assumptions for the Data Models

No	Assumption
1	Strong correlation between long-term animal data and human data
2	Strong correlation between long-term and short-term animal data
3	PAH contribute a known proportion of an overall activity of a mixture
4	Carcinogenic activity of all organic substances in a mixture is known
5	Carcinogenic activity of a mixture as a whole is known
6	Carcinogenic activity of individual components of the mixture is additive
7	Carcinogenic activity of individual mixtures is additive
8	Detailed analytical data for all Source Mixtures are available
9	Detailed analytical data for all Receptor Mixtures are available
10	A mixture from a given source always has the same composition
11	Carcinogenic activity of all mixtures is the same
12	Composition of a mixture at the source and receptor level is the same
13	Source markers for all source mixtures are available
14	Source markers form a fixed proportion of Source and Receptor mixtures
15	Transformation markers are a reliable measure of PAH environmental transformation.
16	It is possible to predict the bioavailability of particle-bound mixture components

2.2.3 Ranking of the models

A robust model is based on valid assumptions. In the real world, however, it is difficult to categorically state, whether an assumption is valid or not. Often, there is not enough high quality data to evaluate an assumption with confidence. An assumption may also be valid or not valid, depending on the exact circumstances under which the assumption is applied. For example, an assumption (no. 2 in table 2) that there is a quantitative correlation between long-term and short-term animal data may hold for nitrosamines, but not for compounds in general [21]. A given assumption may also only approximate the experimentally derived data. For example, an assumption of a linear dose-effect relationship may not be correct at high doses, but on the whole the linear estimation may still offer a reasonable approximation of experimentally derived data. In practice therefore, the models typically depend on assumptions that can be only partially validated and which may hold only imperfectly and under only some circumstances. The validity of a given assumption is expressed as the **Validity Score (V)** The process of deriving the score is outlined in section 2.2.3.1.

The robustness of a given model depends, not only on the validity of its assumptions, but also on the degree to which that model is dependent on each of the assumptions. For example, both the Individual Compound Model and the Monitoring Model depend on assumption #2 from table 2 (Strong correlation between long-term and short-term animal data). Since monitoring is practical only with short-term tests, the Monitoring Model is very dependent on the assumption that short-term tests can predict the potency in the long-term tests. In contrast Individual Compound Model can utilize results from both the long-term and short-term tests, and thus, is less dependent on short-term tests. As a result, the Monitoring Model is much more dependent on the assumption #2 than the individual Compound Model. The dependence of a model on a given assumption is expressed as a **Dependence Score (D)**.

The degree of dependence of a model on its assumption is a property of that model and is not affected by the nature of a compound or mixture (data), to which the model is applied. As a result, it is not necessary or appropriate to change a dependence score when new sets of data are applied to the model. In contrast, the validity of a given assumption is based strictly on the supporting data.

2.2.3.1 Ranking Validity of assumptions

The Validity of an assumption ranges between - 10 points and 0 points. In effect, points are subtracted from 0 ("ideal") to account for deficiencies in the validity of the assumptions.

The score is determined as follows:

For each assumption, the points for each of the applicable statements listed below are summed. A non-applicable statement has a score of 0 points. If there are no data to evaluate the statement, the average of the range is assumed. The assumptions are evaluated on three validity scales: Confidence, Limits and Accuracy. The scoring using these scales is described in the table 3.

Table 3. Scheme for scoring validity of assumptions

Rule no	Category	Score Range	Score Description
1.a	**Confidence** (Quality and availability of data.)	0 to - 3	Not enough reports applicable to test an assumption. Key information is not available.
1.b		0 to - 2	Inconsistencies in the results or poor quality of the data.
2.a	**Limits** (Validity under defined conditions.)	0 to - 1	The assumption may hold only within specified limits.
2.b		0 to - 1	There is evidence, that the assumption does not hold under the "real world" conditions under which the models may be applied.
3.a	**Accuracy** (assumption "approximates" real world situation)	0 to - 1	The assumption involves a relation between the two or more factors (such as dose and response) and the relationship between these factors is not well known.
3.b		0 to - 2	The assumption involves a relation between the two or more factors (such as dose and response) and the relationship between these factors is known and the assumption poorly approximates the relationship within the relevant range.

2.2.3.2 Dependence of models on assumptions

The scoring scheme for the dependence of a model on its assumptions is described below. A score between 0 and 10 is assigned based on the scoring scheme described in table 4.

Table 4. Scheme for scoring dependence of the models on assumptions

Score Range	Score Description
0	Model is independent of a given assumption
1 to 3	Model is somewhat dependent on the assumption, but it is unlikely, that the validity of the assumption will have decisive effect on the robustness of the model.
4 to 7	Model is clearly dependent on the assumption. When the Validity of the assumption is low, the dependence of this model on this assumption counts against it.
7 to 10	Model is critically dependent on the assumption.

Table 5. lists the proposed Dependence Score for three sample models. The same approach is applicable to the models described in section 1.2 or other models defined by a user of this approach. Note that the dependence score provides a convenient summary of the value judgements made during selection of data sets. The other component of the value judgement summary is the set of validity scores for the individual assumptions.

Table 5. Proposed Dependence of models on their assumptions

Assumption Number	Dependence Score		
	Lumped Compound	Sources Mixture	Monitoring Model
1	0	3	10
2	0	1	10
3	0	0	0
4	0	0	0
5	7	10	0
6	0	1	0
7	0	8	0
8	0	8	0
9	0	8	0
10	0	8	0
11	7	0	0
12	0	4	0
13	0	4	0
14	0	4	0
15	0	2	0
16	1	2	10

2.2.3.3 Ranking of robustness of the models

The Validity Scores and Dependence Scores are used to rank the models. Two ranking schemes have been developed (General Rank and Focused Rank). It is advisable to determine both the General and Focused Rank for each model, in order to identify all models which are not suitable for risk assessment of a given group of chemicals.

2.2.3.3.1 Determination of General Rank

Some models are complicated and depend on a number of assumptions. Even if the assumptions are relatively valid, their number tends to reduce the confidence in a model. Source mixture model is an example of such a model (see table 5). There is only one assumption with a Dependence Score of "10", but few assumptions with a score of "0". The General Rank (Rg) is most applicable to such a model.

The General Rank Rg for a given model is determined by summing up the products of the Validity of a given assumption and the Dependence of the model on that assumption (see the equation 4 below).

Equation 4.

$$Rg = \sum_{a=0}^{n} V_a * D_a$$

where:

n	is the number of assumptions considered for a given model
V_a	is the Validity of ath assumption
D_a	is the Dependence of the model on ath assumption
R	is a non - positive number, since V_a is a non - positive number ranging between 0 and - 10 and D_a is a non - negative number ranging between 0 and 10. The more negative the Rank the less robust is the model. Ideally robust model has a Rank of 0.

2.2.3.3.2 Focused Rank

Some models may be dependent on only a few assumptions, but the dependence on these assumptions may be considerable. If the General Rank was used, the model may not fail, because the failings of a few assumptions is offset by independence from other assumptions. Therefore a Focused Rank

(Rf) is used. An example of such a model is the Monitoring Model. The Dependence Scores are "0" for most assumptions, but for a few, the score is "10", indicating heavy dependence.

Focused Rank is determined by summing the Product Score for each assumption. The Product Score for any given assumption is the score assigned to the product of Validity and Dependence for that assumption (see table 6). For example, let us assume, that the Validity of an assumption is - 8 and the Dependence of the model on that assumption is 4. The product of the two numbers is (-8) * 4 = - 32. Table 6 below shows that the Product Score for product between - 30 and - 39 is 1. By summing Product Score for all 16 assumptions, the Focused Rank is determined.

Table 6. Derivation of Product Score from the product of Validity and Dependence.

Product	Product Score
0 to - 29	0
- 30 to - 39	1
- 40 to - 49	3
- 50 to - 59	7
- 60 to - 69	12
- 70 to - 79	18
- 80 to - 100	reject model

2.2.3.4 Selection of models

The models with the least negative score in both the General Rank test and the Focused Rank test are the models that are judged to give the most reliable risk assessment. Some tests perform well in one of the tests but poorly in the other. It is the poorer of the two performances which should be given a higher weighting in priorizing the models. We do not recommend using the results of the two ranking tests in a mechanical manner. The final selection calls for expert judgement and the results from the two ranking tests are a tool to aid in the selection.

3 THE SIGNIFICANCE AND APPLICATION OF OUR APPROACH

Our approach has several useful features. That include:

3.1 Facilitation of literature gathering and analysis

One of the most important features of the described approach is its usefulness in the gathering and analysis of the literature. The US EPA guidelines provide general direction for the types of material that ought to be considered during risk assessment on mixtures. The guidelines do not, however, provide sufficient detail or specificity to direct the literature analysis. In contrast, the described approach defines the specific tasks required to perform the literature analysis in some detail by defining assumptions which need to be tested. Our process thus directs the literature analysis and provides a checklist which assures that the coverage was adequate.

3.2 Formal and simple process for selection of model (s) for subsequent risk assessment

Our approach permits direct comparison of robustness of the approaches to risk assessment. Many different factors are taken into consideration at the same time. In contrast, the US EPA recommends the risk assessment based on mixtures, whenever possible. The US EPA concedes, that under some circumstances, risk assessment based on the individual components should also be considered, but the principles on which to base these value judgements are not well defined.

3.3 Self - documentation of the model selection process.

Performance of the risk assessment calls for frequent value judgements. The results of the assessment are often significantly dependent on the nature of the judgements made. Our approach documents the key value judgements as the Dependency Score and the Validity Score. The reviewer of a document which uses our strategy is thus in a much better position to find what value judgements were made. The US EPA guidelines provide no such feature.

3.4 Facilitated risk assessment process.

Many components of the model selection process are directly reusable and applicable in the risk assessment process. This significantly reduces the "overhead" for the risk selection process.

3.5 Objective evaluation of available options

The structure of the proposed process helps reduce the impact of the personal biases of the investigator (s).

3.6 Versatility - applicable to single compounds, mixtures, exposure assessment

The key activities of the described approach are:

- Define Models
- Compile the list of assumptions for these models
- Generate Dependence Scores for all models and all assumptions
- Generate Validity Scores for all assumptions
- Rank the models based on the Dependence and Validity Scores.

This approach can be applied to single compounds as well as complex mixtures and it can be applied to the exposure assessment modeling as well.

3.7 Modular - facilitates team effort

The bulk of the work in this process involves evaluating the validity of assumptions. Evaluation of each assumption represents a discreet task which can be assign to different members of the team. This approach lends itself to teamwork well

4 APPLICATION OF THE APPROACH TO A SET OF DATA - AN EXAMPLE.

In order to apply the approach to any specific set of data, the scoring of the assumptions must be completed. Our group is not yet ready to do this scoring. **For demonstration purposes only, a set of scores has been created and presented in table 6. THESE SCORES DO NOT REPRESENT THE MINISTRY'S SCORES FOR THE PAH AND THE PAH-CONTAINING MIXTURES.** The purpose of this exercise is to illustrate the process and demonstrate the interpretations possible with this approach.

The steps involved in ranking the models are described bellow:

4.1 Define models and their dependence on assumptions

The models are described in section 1.2 and the Dependence Scores are summarized in table 5.

4.2 Determine the Validity Score for the assumptions

A simulated Validity Scores were derived for each assumption (see table 2) using the scoring scheme defined in table 2. An example of the derivation of the Validity Score is presented in table 7. The individual scores under each scoring category (table 7) are summed up to give the Validity Score. The validity score was simulated for the other assumptions in a similar way as the Validity Scores are presented in table 7.

Table 7. Derivation of simulated Validity Scores for assumption #2.

Category	1.a	1.b	2.a	2.b	3.a	3.b	Validity Score
Score	-2	-1	-1	-1	0	-2	-7

Table 8. Simulated Validity Scores for assumptions.

Assumption number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Validity Score	-3	-7	-4	-5	-3	-7	-3	-3	-3	-8	-4	-3	-7	-5	-5	-4

4.3 Determine the products of Validity Scores And Dependence Scores for each model.

The products (Pg) of Validity Scores (Va) and Dependence Scores (Da) are required to calculate both the General Rank and the Focused Rank. The products were obtained as described in section 2.2.3.3.1. and summarized in table 9.

4.4 Determine the General Rank

In order to calculate the General Rank, the products for each assumption in the model were summed up. General Rank score for three sample models is presented in the "Rg" row of table 9.

4.5 Determine the Focused Rank

In order to calculate the Focused Rank, the products (Pg) were first converted to Product Scores using table 6. The Product Scores for each assumption in the model were then summed up, in order to obtain Focused Rank. Focused Rank score for three sample models is presented in the "Rf" row of table 10.

4.6 Evaluation of Results

In the specific (simulated) example, the best model is clearly the Lumped Compound model, which performed best of the three models considered in both the General Rank and the Focused Rank Test. It is instructive to look at the differences between the performance of the models in the two ranking schemes. The Source Mixture model is dependent on a large number of assumptions, but the assumptions are either relatively valid, or the model has low dependence on them. This model received the worst score in the General Rank test, because of its dependence on large number of assumptions. In contrast, the model did well in the Focused Rank test, because of its low dependence on any of the assumptions. In contrast, Monitoring model is dependent critically on a few assumptions, which, in our simulation were not very valid. As a result, it performs better in the General Rank test then in the Focused Rank test, even though it does poorly in the Focused Rank test.

In general, both the Focused Rank and the General Rank answer different questions and should be used in parallel.

Table 9. Dependence Scores (Da) and Simulated Validity Scores (Va) and their products (Pg) for three sample models. The table also provides the General Rank (Rg) and the Focused Rank (Rf) for the three models

Ass.	V_a	Lumped Mixtures		Source Mixture		Monitor.	
		D_a	Pg	D_a	Pg	D_a	Pg
1	-3	0	0	3	-9	10	-30
2	-7	0	0	1	-7	10	-70
3	-4	0	0	0	0	0	0
4	-5	0	0	0	0	0	0
5	-3	7	-21	10	-30	0	0
6	-7	0	0	1	-7	0	0
7	-3	0	0	10	-30	0	0
8	-3	0	0	8	-24	0	0
9	-3	0	0	8	-24	0	0
10	-8	0	0	7	-56	0	0
11	-4	7	-28	0	0	0	0
12	-3	0	0	4	-12	0	0
13	-7	0	0	4	-28	0	0
14	-5	0	0	4	-20	0	0
15	-5	0	0	2	-10	0	0
16	-4	1	-4	2	-8	10	-40
Rg			-53		-265		-140
Rf			0		9		22

Table 10. Simulated General and Focused Ranks (Rg and Rf respectively) for different models. Order of preference based on each rank is given in the columns labeled "Order".

Model	General Rank		Focused Rank	
	Rg	Order	Rf	Order
Lumped mixtures	-53	1	0	1
Source mixtures	-265	3	9	2
Monitoring	-140	2	22	3

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A9 Dose Response for Selected Environmental Air Pollutants: Results from a Study on Runners;

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INTRODUCTION

The cardio-respiratory benefits of exercise have been well documented. However, there has been less attention directed towards the risk potential for adverse health effects of inhaled pollutants while exercising outdoors, particularly in urban environments. In assessing the effects of air pollutants on exercising individuals, consideration must be given to 1) the ambient air conditions (type and concentration of pollutants), 2) the intensity and duration of exercise being undertaken, 3) environmental factors, and 4) the age, level of fitness and presence of any underlying disease of the person exercising. Furthermore, the risk may be increased for the city runner, because a high ventilation rate is often combined with close exposure to traffic. However, air pollution mixtures are very complex, varying in both constituents and levels at any given time. Many pollutants have not been demonstrated to have significant effects on the exercising individual, or have not been systematically examined with respect to their impact. This study examines effects of a number of pollutants on runners.

METHODS

Seventy (54 M, 16 F) members of the Longboat Roadrunners Club, a group of some 160 runners, have been tested on Wednesday evening (5:30 PM) over 75 weeks (1986-1988), when their 6-10 mile (10-16 km) running route follows the downtown core and the crowded Lakeshore transportation corridor, where there is a potential for heavy exposure to vehicle exhaust. The average age of the runners was 37 yrs and ranged from 17 to 57 yrs, the male runners being slightly older (38 yrs) than the female runners (34 yrs). The pulmonary function test results indicated that the runners were very healthy.

Sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and respirable particulate matter were measured using sampling systems designed, constructed and used in the past at The Gage Research Institute (1-5). These samplers are small, portable, multi-pollutant samplers driven by a battery-operated pump system. The particulate sampling consists of a cyclone and filter cassette assembly, operated at a flow rate of 1.7 L/min, yielding a 50% particle cut of 5 microns (6). The gas systems for NO_2 and SO_2 each use 2 impingers in parallel (with one teflon inlet) containing appropriate absorbing solutions, operated at 1.0 L/min (500 ml/impinger). SO_2 concentration is assessed by the West and Gaeke method (7), and the U.S. EPA NAAQS (8). The NO_2 concentration is assessed by the TGS-ANSA method (9).

Samplers were carried on 2 bicycles (mobile samplers) to assess "personal exposure"; one bicycle followed alongside a group that ran 6 miles (10 km), the other bicycle followed alongside a group that ran 10 miles (16 km). Gage stationary samplers were also located at a central Ontario Ministry of the Environment (MOE) monitoring network site at 26 Breadalbane St., Toronto.

In order to assess "personal exposure", 2 portable electrochemical carbon monoxide (CO) monitors (Industrial Scientific, model CO-260) were used. One was carried on each bicycle and recordings were taken at various sites along the route (Table 2).

Data were also obtained from the MOE air pollution monitoring network (ozone, SO_2, CO, oxides of nitrogen, suspended particulate matter) at their Breadalbane site. Temperature and relative humidity were obtained from The Atmospheric Environment Services (AES), at their Trinity College site. A temperature/humidity monitor (Jenway, model 5500) using a wet bulb/dry bulb system with air pump was carried on the Gage 10 mile bicycle and readings taken at 4 points along the route.

Spirometric tests of lung function were made pre and post run using two Med-Science Wedge spirometers. Tests were administered according to standard procedures (10).

Immediately after training runs, runners were asked to subjectively rate a number of symptoms, and the air pollution levels on the running route, using a modified Borg scale ranging from 0 (no symptom or pollution) to 10 (very, very strong, almost maximum).

The relationships between the environmental variables such as NO_2 and temperature, and the response variables, which included the symptom and the pulmonary function variables were investigated using multiple regression methods.

Backward stepwise linear regression was employed to assist in the identification of those combinations of environmental variables that best predicted the response variables. All regression models included as a factor each runner's ID code. Therefore, all relationships identified were between days within runners, i.e. taking into account events within individuals. The final model, using backward stepwise regression, had the lowest Mallow's CP statistic (11) that best predicted the response variable. After identifying the number of variables that the model might have using backward stepwise regression, a regression analysis on all possible combinations of the same number of variables selected from the original list of variables was performed. This permitted the identification of other models that would have been missed by the stepwise procedure, but are biologically meaningful, and only slightly less statistically powerful.

Results

Table 1 shows mean pollutant concentration recorded by the Gage mobile samplers (6 and 10 mile), the Gage-Breadalbane site stationary samplers, and the MOE-Breadalbane monitoring station.

For NO_2, the maximum levels recorded ranged from 50 to 60 parts per billion (ppb) for the 4 "sites", and the Gage 6-mile mean concentration was slightly higher than the other 3 "sites". Mean sulphur dioxide levels were all below 10 ppb and maximum values were less than 35 ppb. For carbon monoxide and respirable suspended particulate (RSP) matter, the Gage 6-mile values were higher than the Gage-10 mile values, and the MOE stationary site underestimated the exposure of the runners.

Table 2 shows mean CO concentration at sites along the 10 mile running route. With four exceptions, CO at each site along the route is higher on the way out than on the way back, even though the runners followed the same route out and back. These differences can be explained by the vehicular traffic burden, with peak traffic occurring during the "out" CO recordings, while during "back" recordings the "rush hour" traffic has decreased. Data from the 6 mile bicycle showed a similar trend to the 10 mile bicycle.

The results of the stepwise regression analysis for the exposure and symptom variables shown in Table 3 utilize the pollutant concentrations measured by the Gage personal samplers that were placed on the bicycles that accompanied the runners on their route. The response variable sore/dry throat is related negatively to the predictor variable average relative humidity (AVRH). The variable breathing fatigue is positively related to temperature. The pollution rating scale is shown to be strongly related to NO_2, mean CO and temperature. Relationships of air pollutant concentrations to pulmonary function were not as strong as to pollution rating and symptoms.

The effect of replacing the estimates of CO and NO_2 obtained by using the Gage portable samplers, by the corresponding estimates obtained from the MOE-Breadalbane station was investigated, for the response variable pollution rating (Table 4). When the CO estimate obtained from the Gage portable sampler (Model A) was replaced by the MOE-

Breadalbane estimate (Model B), the regression coefficient became non-significant. Therefore, the statistically significant positive relationship between Gage CO and the pollution rating became negative and nonsignificant when the Gage CO was replaced by the Breadalbane - CO.

DISCUSSION

Pollutant levels were reasonably low, with maxima being 17-41% of the 1-hr average Ontario Ambient Air Quality Criteria. The results show that using the MOE values measured at the stationary fixed site remote from the running route would underestimate the runners "personal" exposure. Also, the 6 mile and 10 mile runners were exposed to different mean concentrations. These findings illustrate the importance of using "personal" sampling when assessing exposure of mobile subjects. A possible explanation for the difference in mean 6 and 10 mile levels is that the 10 mile route extends out along the Martin-Goodman bicycle/jogging trail, between Lake Ontario and Lakeshore Boulevard. Traffic is lighter and less congested there compared to the downtown core, also it is more open (parkland with few buildings) and on-shore breezes may "clean" the area. Furthermore, the 10 mile group returns to the downtown core approximately 1/2 hour later than the 6 mile group, when rush hour traffic is reduced and pollution concentrations are lower, as suggested by lower CO concentrations that were recorded on the return route. Therefore, the 6 mile runners, who spend more of their time in the downtown core compared to the 10 mile group, may be exposed to higher pollution concentrations, although the actual pollutant dose or burden may be similar for the 2 groups, as the 10 mile group is exposed for a longer time.

It was found that the runners' subjective rating of pollution was jointly related to breathing fatigue, eye irritation and sore/dry throat (not shown), suggesting that the subjects' symptom reporting was related to their perceptions of the pollution levels they were exposed to. The results of the present study suggest that symptom reporting may be a sensitive or subtle indicator of effects of air pollutants, and that the subjects' perception of pollution levels may be an integrator of the symptom complex that results from exposure.

The observed relationship between the subjective rating of pollution and the local concentrations of NO_2 and CO, suggests that the pollution rating may be a reflection of, or influenced by, local car exhaust emissions. While NO_2 and CO, by themselves, may not cause the symptoms, they may be indicators of car exhaust emissions, and the actual irritant response may be to car exhaust emissions that we are not measuring locally (with the personal samplers). Similarly, peak CO concentration may be an indicator of "pockets" of car exhaust emissions, and these would not likely be picked up by remote, fixed-site MOE monitoring. Therefore, the fact that relationships are strongest and most consistent with the mobile or "personal" concentrations, and variably, inconsistently, or not at all related to the levels measured at the fixed remote sites, emphasizes the importance of measuring exposure as close to the subjects as possible.

In summary, the results suggest that symptoms and subjective rating of severity of pollution are related to pollution levels; the strongest relationships are seen using levels measured by the mobile personal samplers.

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TABLE 1

MEAN POLLUTANT CONCENTRATIONS

1987 & 1988
(N=34 weeks)

POLLUTANT (SITES)	MEAN ± SD*	RANGE**
NO_2 (Gage - 6 mile)	36 ± 10	16 - 60
NO_2 (Gage - 10 mile)	31 ± 10	9 - 52
NO_2 (GAGE - Breadalbane)	29 ± 9	14 - 50
NO_2 (MOE - Breadalbane)	28 ± 14	0 - 55
SO_2 (Gage - 6 mile)	4 ± 6	0 - 29
SO_2 (Gage - 10 mile)	4 ± 5	0 - 25
SO_2 (GAGE - Breadalbane)	5 ± 8	0 - 28
SO_2 (MOE - Breadalbane)	6 ± 10	0 - 35
CO (Gage - 6 mile)	3.3 ± 1.6	0.8 - 7.4
CO (Gage - 10 mile)	2.1 ± 1.4	0.4 - 7.2
CO (MOE - Breadalbane)	0.9 ± 0.8	0.0 - 4.0
RSP (Gage - 6 mile)	84 ± 40	8 - 159
RSP (Gage - 10 mile)	62 ± 18	22 - 93
RSP (GAGE - Breadalbane)	42 ± 20	7 - 110

* Mean ± standard deviation. ** Range: lowest to highest level. NO_2 and SO_2 in parts per billion (ppb). Gage-6 mile time-weighted average (1730 -1830 hrs), Gage-10 mile time-weighted average (1730-1900 hrs), Gage-Breadalbane time-weighted average (1700-1900 hrs), MOE-Breadalbane, Ontario Ministry of the Environment (MOE) pollutant monitoring site-downtown Toronto average of (a) mean of 12-5 minute averages 1700-1800 and (b) mean of 12-5 minute averages 1800-1900 hrs; CO in parts per million (ppm), Gage-6 mile & Gage-10 mile average of 12 sites and 18 sites respectively, out & back along the route, MOE Breadalbane as above for NO_2 and SO_2; RSP in $\mu g/m^3$, RSP Gage-6 mile, Gage-10 mile & Gage-Breadalbane time-weighted average as above for NO_2 and SO_2. Data reported only if complete for all sites.

TABLE 2

MEAN CO CONCENTRATIONS FOR SITES ALONG 10 MILE WEDNESDAY RUN ROUTE OVER 1986 - 1988

Site	Out (weeks)	Back (weeks)
University Settlement House	1.4 ± 1.9 (71)	1.0 ± 1.4 (65)
Queen and Soho	5.3 ± 8.3 (69)	2.8 ± 2.5 (68)
King and Peter	4.4 ± 4.3 (71)	1.7 ± 1.6 (66)
Wellington and Peter	3.2 ± 4.1 (16)	1.5 ± 2.1 (20)
Front and Peter	6.0 ± 6.3 (54)	2.7 ± 2.4 (32)
Front and Spadina	8.3 ± 7.5 (68)	4.5 ± 3.4 (65)
Front and Portland	1.0 ± 1.1 (25)	1.1 ± 1.7 (21)
Spadina Bridge underpass	4.0 ± 2.8 (44)	2.8 ± 2.5 (45)
QEW and Spadina	8.4 ± 5.2 (45)	5.1 ± 3.8 (41)
Bathurst Bridge overpass	3.0 ± 2.9 (27)	1.2 ± 1.1 (22)
Queen's Quay and Spadina	4.7 ± 3.6 (41)	4.4 ± 6.2 (26)
Canada Malting	1.6 ± 1.6 (24)	3.3 ± 2.8 (24)
Lakeshore and Bathurst	3.6 ± 2.9 (27)	3.4 ± 4.3 (25)
Tip Top Taylors (Lakeshore)	2.2 ± 2.3 (53)	1.6 ± 4.7 (53)
War Plane at Ontario Place	0.8 ± 1.4 (55)	1.0 ± 1.2 (54)
Remembrance Dr.(3 mile turn)	1.8 ± 2.0 (73)	1.6 ± 1.6 (70)
Lakeshore Blvd. (bleachers)	1.6 ± 2.1 (70)	1.4 ± 1.7 (68)
Aquatic Drive	1.1 ± 1.4 (71)	0.9 ± 1.2 (68)
Tennis courts (4 mile turn)	1.3 ± 1.4 (54)	1.1 ± 1.5 (54)
Boulevard Club	1.5 ± 1.6 (71)	1.3 ± 1.6 (66)
Budapest Park	1.0 ± 1.5 (54)	1.0 ± 1.4 (53)
Sunnyside Pool (5 mile turn)	1.5 ± 2.2 (70)	0.8 ± 1.0 (11)
Mean CO concentration (ppm) (all sites averaged)	3.2 ± 2.0 (73)	2.1 ± 1.5 (73)
Peak CO concentration (ppm)	12.7 ± 9.4 (73)	7.6 ± 5.6 (73)

Mean CO concentration - all sites out and back:
2.7 ± 1.6 ppm (73)

TABLE 3

MULTIPLE REGRESSION EQUATIONS FOR SYMPTOMS AND EXPOSURES OBTAINED FROM BACKWARD STEPWISE MULTIPLE LINEAR REGRESSION

$$\text{SORE/DRY THROAT} = -0.014 \times \underset{(0.002)}{\text{AVRH}}$$

$$\text{BREATHING FATIGUE} = 0.019 \times \underset{(0.04)}{\text{AVTEMP}}$$

$$\text{EYE IRRITATION} = 0.005 \times \underset{(0.12)}{NO_2} - 0.10 \times \underset{(0.08)}{\text{MEANCO}} + 0.024 \times \underset{(0.02)}{\text{PEAKCO}}$$

$$\text{POLLUTION RATING} = 0.009 \times \underset{(0.001)}{NO_2} + 0.14 \times \underset{(0.002)}{\text{MEANCO}} + 0.049 \times \underset{(0.0001)}{\text{AVTEMP}}$$

AVRH - average relative humidity (%). AVTEMP - average temperature (°C). MEANCO (ppm) - all sites out + back. PEAKCO (ppm) - highest CO among all sites out + back. NO_2 ($\mu g/m^3$). Breathing fatigue N=491. All others N=423.

TABLE 4

MULTIPLE LINEAR REGRESSION MODELS FOR THE SUBJECTIVE POLLUTION RATING SCALE AGAINST MEAN NO_2, CARBON MONOXIDE AND TEMPERATURE

MODEL A	REGRESSION COEFFICIENT	P VALUE
NO_2 - GAGE	0.0086	0.0017
TEMPERATURE - GAGE	0.0476	0.0001
CO - GAGE	0.1235	0.0071
MODEL B		
NO_2 - GAGE	0.012	0.0001
TEMPERATURE - GAGE	0.038	0.0001
CO - BREADALBANE	-0.084	0.31

NO_2 - GAGE AND CO - GAGE are the measurements of NO_2 ($\mu g/m^3$) and carbon monoxide (ppm) concentrations using the Gage portable samplers transported on the bicycles.

CO - BREADALBANE is the measurements of carbon monoxide concentrations (ppm) made by the Ministry of the Environment at their Breadalbane location.

A10

INVESTIGATION OF SHORT-TERM MUTAGENICITY AND CHEMICAL COMPOSITION OF THE ORGANIC SOLVENT EXTRACTABLE FRACTION OF COKE OVEN EMISSIONS

BY

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Introduction

This study represents the conclusion of ORTECH's part of an ongoing investigation, the objective of which was to determine if a practical ambient air standard for PAH is possible based on mutagenic activity. It was not the intention of this study to suggest controls for coke oven operations. The coke oven testing loctions chosen were selected to obtain large amounts of PAH's for tiered biological tests. The samples were collected at three Ontario coke oven operations.

Background

The potential environmental hazards of PAH's are well known. PAH's are the largest group of chemical carcinogens found in airborne particulates. Coke workers have been singled out from other by-product workers as having the highest incidence of lung cancer. It is alleged that the cause for this is exposure to PAH compounds present in the emissions generated during the coking process.

Phase I of this program concentrated on the sampling protocol and analytical methods used to collect and analyze coke oven emissions. The sampling program included direct sampling of a coke oven during the entire coking cycle by means of a hole drilled through the coke oven lid (LID samples).

These samples represent the worst cases and were collected to insure suficient material would be available for all subsequent tests. At the same time, samples were also collected on top of the coke ovens (Coke Oven Top Side Samples - COTS) during the entire coking cycle. These samples represent the environment on top of the coke ovens that had previously been linked to health effects. Each sample set included a large sample which was collected using a high volume (Hi-Vol) sample backed up with polyurethane foam plugs plus a low volume (Lo-Vol) sample collected concurrently. COTS samples had three Hi-Vol filters with foam backup and two Lo-Vol filters to ensure sufficient sample was collected. Coefficient of Haze (COH) was also measured on the coke oven top. This enabled correlation analyses to be conducted between the Hi-Vol and Lo-Vol samples for selected parameters that were measured, specifically the total particulate matter (TPM) and the soluble organic fraction (SOF) of the TPM. The SOF of both LID and COT sample were tested for mutagenicity using the AMES assay.

During Phase II, selected samples from Phase I were used to define and quantify the chemical composition of the coke oven emissions and relate these results to the mutagenicity of the unfractionated samples. This was accomplished using a fractionation scheme to separate the complex mixtures into well defined sub-fractions to better isolate the mutagenicity and chemistry.

Results and Discussion

The collected samples provided information that was used to establish the relationship between Hi-Vol and Lo-Vol samples for TPM and SOF. This presentation discusses the relationships obtained.

The plots presented show the data and the results of simple regression analysis performed using LOTUS 123's data regression function. The solid line represents this regression line calculated for the data. The regression was forced through zero as no weight gain by the filters without sample collection was anticipated. The coefficient of determination (R-squared) is also shown.

Data relating to total particulate matter (TPM) and soluble organic fraction (SOF) were determined for LID and COTS samples. Dichloromethane (DCM) was the extraction solvent used for the Hi-Vol samples to give DCM-SOF. Benzene was the solvent used to extract the Lo-Vol samples. The Lo-Vol/SOF was a benzene soluble fraction of the total particulate matter (BSFTPM) and represents a benchmark to link our results with epidemiological study data and existing occupational standards.

Samples collected at the three different mills established that a good relationship existed between Hi-Vol and Lo-Vol sampling methods. A linear relationship was established for TPM and SOF for both LID and COT samples.

An important aspect of this study was to determine whether a correlation exists between the SOF of TPM and AMES mutagenicity assays. Mutagenic activity is expressed as the specific activity which is determined as revertants per microgram of sample. The mutagen density which corresponds to the amount of mutagenic material per cubic metre of air at the sampling location was used for the purpose of correlation analysis. The mutagen density is a product of the specific activity for a Salmonella tester strain (revertants/μg) and weight of SOF/m^3 of air.

A linear relationship was observed between mutagen density for TA-98 with metabolic activation and the SOF (mg/m^3) of the collected emissions. LID samples gave a value for R-squared of 0.91 while the value of R-squared for the COT samples was 0.81. Furthermore, the chemical identification evidence determined on the various fractions of the SOF, showed that the major part of the mutagenic response was detected for the PAH fraction.

Phase II of this program addressed the isolation of mutagenicity using a fractionation approach and identification of chemical classes responsible for mutagenicity in the SOFs.

The fractionation procedure used to collect specific separated chemical class fractions was validated using mixtures of known substances representative of the individual chemical classes. Five (5) fractions were collected and the majority of the mutagenicity determined for the unfractionated SOF could be accounted for by the mutagenicity of the PAH fraction. The chemical analysis of the various fractions resulted in the tentative identification of approximately 80 chemical componds, the majority of which were PAH's. The PAH fraction contained the neutral PAH and consisted mainly of parent and alkyl substituted PAH compounds. The aza-arene type PAH species were present in fraction #3. The other fractions with the exception of Fraction 1 showed some mutagenic response. The sum of the calculated mutagen densities for the various fractions (Mill #1-LID) was not significantly different from the value obtained for the unfractionated SOF. The LID-PUF and the COTS samples showed close agreement with the higher molecular weight range PAHs e.g. 228-252, with a greater disparity for the lower molecular weight range PAHs e.g. 166-202.

In general, the PAH-COT fractions gave lower specific activities for the parent PAHs than for the corresponding LID and LID-PUF fractions. The specific activities for the COT samples was also lower than for the corresponding LID and LID-PUF fractions. This evidence suggests the existence of a relationship between the parent PAH and mutagenicity. A large increase in the amount of alkylated PAH was observed in the PAH-COT fractions when compared to the LID and LID-PUF fractions. The specific activity of the COTS sample was lower than for the corresponding LID and LID-PUF samples. This evidence suggests alkylated PAHs do not contribute to the mutagenicity found in the fractions. From this study, it is not possible to conclude which individual PAH or combination of PAHs was responsible for the mutagenicity of the coke oven emissions.

A11

GENOTOXIC COMPOUNDS ASSOCIATED WITH RESPIRABLE URBAN AIR PARTICULATE. CHEMICAL FRACTIONATION AND BIOASSAY OF COMPLEX MIXTURES. B.E. McCarry[1], D.W. Bryant[2] and D.R. McCalla[2], Departments of Chemistry[1] and Biochemistry[2], McMaster University, Hamilton, Ontario L8N 3Z5. MOE Project No. 386G

INTRODUCTION

The objective of this research program is to examine PAH and PAH derivatives adsorbed to respirable urban particulate and to assess the potential health hazard they present. To achieve our goal of detecting airborne genotoxins, we have used a class-selective chemical fractionation procedure coupled with an analysis of the fractions by a combination of chromatographic methods and mutagenicity assays. This approach focuses attention first on the genotoxic activity of each fraction then subsequently on the compounds within that fraction that are responsible for that genotoxic activity.

Nearly three thousand chemical species have been identified in the earth's atmosphere (Graedel, et al., 1986). The chemical analysis of organic extracts of total suspended respirable particulate has been extensively reported (Butler et al., 1987; Hoff and Chan, 1987; Yamauchi and Handa, 1987; Daisey et al., 1986; Greenberg et al., 1985). Surprisingly few of these identified chemicals have been examined using short term bioassay tests (STTs). While the value of SSTs for the prediction of chemical carcinogenicity varies with the class of compound (Ashby, et al., 1989; Piegorsch and Hoel, 1988), these tests remain the most direct method for assessing a chemical's genotoxicicity and thus its potential carcinogenicity. While these biological techniques can be extremely sensitive with individual compounds (eg. the probability for detection of a nitroaromatic carcinogen is 0.9), their sensitivity for other aromatic carcinogens varies.

MATERIALS AND METHODS

Air particulate samples were of two types: TSP (General Metal Works L-2000 H) with flow controller set at 40 ft^3/min (1630 m^3/24h) and PM10 (selected for respirable particulate less than 10 μm in diameter). All suspended particulate samples were collected on Teflon/glass fibre filters (Pallflex 8 x 10 inch type TX40H120WW). Samplers were sited at two locations in Hamilton: Downtown located on the roof of an OME station #29000 at the intersections of Kelly and Elgin Streets, and Westdale (Station # 29118) at the intersection of Main St West and the exit of Highway 403).

Table 1: COMPARISON OF PM10 RESPIRABLE PARTICULATES BY LOCATION

	Average Load: (24h, 40cfm)	Maximum	Minimum
Downtown (Kelly)	0.089844g (0.052616)[1]	0.326600	0.019950
Westdale (Main W)	0.062679g (0.032883)	0.146700	0.017650

[1]Standard deviation N= 85

Sample loadings of respirable particulate varied with the site (Table 1). On average Westale, received seventy percent of the total respirable particulate that was measured at the downtown site on the same days. At the Downtown location where both PM10 and hi-vol units were located, the respirable particulate averaged 62% of the total suspended particulate (0.144223g (.0814) N= 83).

PARTICULATE EXTRACTION METHODS:

Filters collected for a designated period or atmospheric condition were pooled and extracted with dichloromethane (DCM) and methanol (MEOH) in a soxhlet apparatus for 16h. The organic extract was fractionated according a scheme that has been described (Figure 1, McCalla, et al., 1988). Sequential elution of a neutral alumina column with solvents of increasing strength yielded the following fractions: [A1] (hexane), [A2] (benzene), [A3] ($CHCl_3$/1% methanol), [A4] (methanol), [A5] (methanol/water) and [A6] (water). Fractions [A2] and [A3] as well as [A4] and [A5] were pooled to yield fractions [A23] and [A45]. Aliphatics which were a major contaminant in [A23] were removed by chromatography on Sephadex LH20.

Atmospheric conditions monitored continuously during sampling (Ontario Ministry of Environment West Central Region, F. Dobroff) included nitrogen dioxide (NO_2), oxides of nitrogen (NO), sulphur dioxide (SO_2), carbon monoxide (CO), ozone (O_3), and coefficient of haze (COH). Wind direction and wind speed were also monitored (Woodward #29026).

BACTERIAL ASSAYS:

The Salmonella typhimurium/microsome assays for mutagenic activity with or without Araclor 1254 induced rat liver S9 (4%) were performed as described by Maron and Ames (1983). Tester strains were supplied by B.N. Ames (TA98) or M. Watanabe (TA1538/NR[pYG111] and TA1538/DNP[pYG122]).

DNA ADDUCT ASSAYS:

TA1538(pYG122) ($3x10^9$ cells) were treated with various fractions of organic extracts prepared from air particulates. After treatment DNA was extracted, digested and enriched for nonpolar nucleotide adducts. The ^{32}P-ATP postlabelling procedure used was as described by Randerath et al. (1985) and Gupta (1986). Labelled adducts separated on PEI cellulose TLC plates were quantified using liquid scintillation counting. Relative adduct labelling (RAL) was calculated according to described methods.

RESULTS:

Table 1 shows the mutagenic activity found in the crude alumina fractions from the pooled Spring, 1989 filters. Mutagenic activity, expressed as revertants per m^3 air, was determined from dose response curves (five doses, duplicate assays). Three strains of Salmonella typhimurium were compared for their response to the material extracted from the particulates. Virtually all detectable mutagens were divided between the two pooled eluent fractions [A23] and [A45].

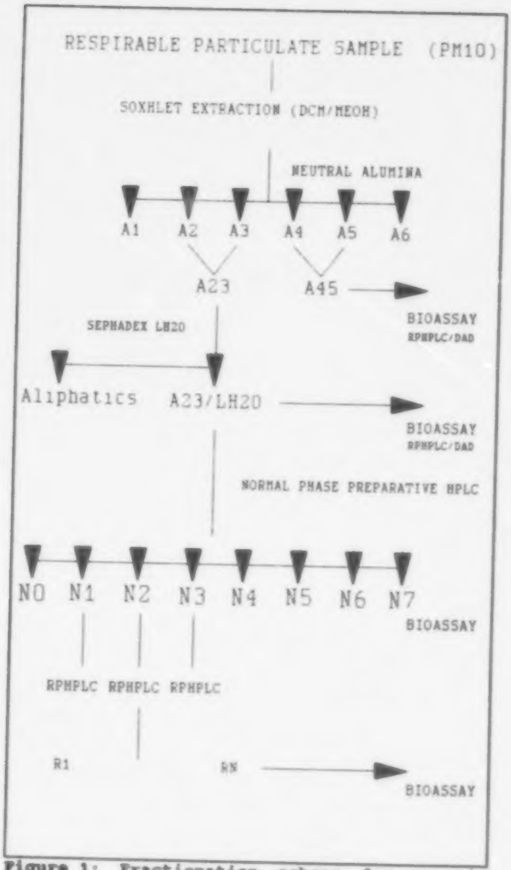
RESPIRABLE PARTICULATE SAMPLE (PM10)
SOXHLET EXTRACTION (DCM/MEOH)
NEUTRAL ALUMINA
A1
A2
A3
A4
A5
A6
A23
A45
BIOASSAY
RPHPLC/DAD
SEPHADEX LH20
Aliphatics
A23/LH20
BIOASSAY
RPHPLC/DAD
NORMAL PHASE PREPARATIVE HPLC
N0
N1
N2
N3
N4
N5
N6
N7
BIOASSAY
RPHPLC
RPHPLC
RPHPLC
R1
RN
BIOASSAY

Figure 1: Fractionation scheme for organic extract of particulates.

Table 2: COMPARISON OF MUTAGENICITY VALUES

REVERTANTS PER M^3 OF AIR DATE/TYPE OF FILTER	FRACTION [A1]	[A23/LH20]	[A45]	[A6]
Spring: 1989 Teflon: Hi-vol				
TA98 -S9	0.08	1.05	3.38	0.08
TA98 +S9	0.03	3.32	2.68	0.00
TA1538/DNP(pYG122)-S9	0.06	3.06	4.96	0.32
+S9	0.01	7.86	7.47	0.50
TA1538/NR(pYG111)-S9	0.60	1.56	3.16	0.00
+S9	0.0	5.57	6.69	0.53

All mutagenic activity was recovered after the passage of [A23] through Sephadex LH20 (a step used to remove non-mutagenic aliphatics). Both **DIRECT AND INDIRECT** acting mutagens (-/+ S9) were about equally divided between these two fractions [A23]LH20: 43.5%; [A45]: 42.7% without S9; [A23]LH20: 49.9%; [A45]: 43% in the presence of S9 microsomal activation.

Table 3: [B] FRACTIONS FROM SPRING 1989: RECOVERY OF MUTAGENIC ACTIVITY.

Revertants per cubic meter of air:

FRACTION	(pYG122)		(pYG111)		TA98	
	-S9	+S9	-S9	+S9	-S9	+S9
[B1]	0.16	0.5	0.37	0.46	0.23	0.26
[B2]	5.23	4.67	3.09	7.01	1.06	2.26
[B3]	0.77	0.42	0.45	0.40	0.28	0.32
[B4]	0.95	0.84	0.46	0.70	0.34	0.34
[B5]	0.15	0.18	0.21	0.50	0.18	0.21
[B6]	0.24	0.12	0.32	0.55	0.17	0.07
[B7]	0.62	1.37	0.51	1.29	0.45	1.19
TOTAL	8.12	8.10	5.42	10.91	2.71	4.64
MUTAGENIC YIELD [A23]/LH20('89):						
	3.05	7.85	1.56	5.57	1.05	3.32
PERCENT RECOVERY AFTER FRACTIONATION:						
	266	103	347	196	258	140

These results clearly indicate that most detectable mutagens are found in the classical PAH and PAH derivatives in [A23]LH20 fraction. A significant quantity of the total mutagenicity resides in compounds which may be characterized as polar PAH derivatives in [A45].

The [A23]LH20 pooled material was further divided into eight fractions (N0..N7) by **normal phase** chromatography as shown in Table 3. The selection of cut points for N fractions was based both on the distribution of mutagenic activity and on chemical class: N1 - PAH, polycyclicaromatic furans and polycyclic sulphur compounds; [N2] - nitro-PAH; [N3] - dinitro-PAH and polyaromatic quinones; [N4] to [N6] - polyaromatic ketones phenols and quinones; [N7] - polyaromatic nitrogen compounds (McCalla *et al.* 1988).

Fraction [N1], which contained PAH including coronene, was relatively inactive in terms of mutagenic activity. The [N2] fraction constituted up to 64% of the direct-acting [(pYG122)-S9] and 64% of the indirect-acting [(pYG111)+S9] mutagenic activity, irrespective of the strain used for analysis. Modest levels of mutagenicity were found in fractions [N3], [N4] AND [N7], and low levels in fractions [N1], [N5] and [N6]. No significant mutagenic activity was found in [N0]. Air particulates collected during the Summer of 1988 produced a somewhat different pattern of mutagenic activities; the bulk of the direct-acting mutagenic activity in Summer 1988 fractions was found in [N2] and [N3].

Reverse phase chromatography of the [N2] fraction from the summer months of 1988 resulted in the mutachromatograms shown in **Figure 2** (fractions were collected at thirty second intervals). In these experiments, the fractionated eluent from analytical reverse phase chromatography was tested directly with the three strains TA98, (pYG111) and (pYG122). The results for [N2] confirm that all the strains detect more or less the same mutagenic components with differing sensitivities. TA1538/NR(pYG111) detected approximately 3.5 times more mutants compared to TA98.

The strain TA1538/DNP(pYG122) which was selected for its strong response to dinitropyrenes, reacted with only a few fractions of [N3]. We conclude that a very narrow range of compounds is responsible for all the direct acting mutagenicity of [N3], possibly dinitropyrenes (results not shown).

POLAR MUTAGENS IN ALUMINA FRACTION [A45]

Fully 50% of the total mutagenic activity of the Spring 1989 extract was located among the polar compounds which fall into the [A45] alumina fraction. The sample was fractionated by normal phase chromatography (M9-PAC) into fractions (A0) through (A3) using a linear gradient of 100% dichloromethane to 100% ethanol over forty minutes at a flow rate of 4.2 mL/min. The data in Table 5 indicate none of the strains showed a preferentially enhanced sensitivity. (A0) and (A1) contain polar PAH rich in nitro derivatives or which require reduction and/or acetylation for conversion to mutagenic electrophiles. The addition of S9 doubles the mutagenic response in all the tester strains. Recoveries of material show no substantial losses or synergistic relationships.

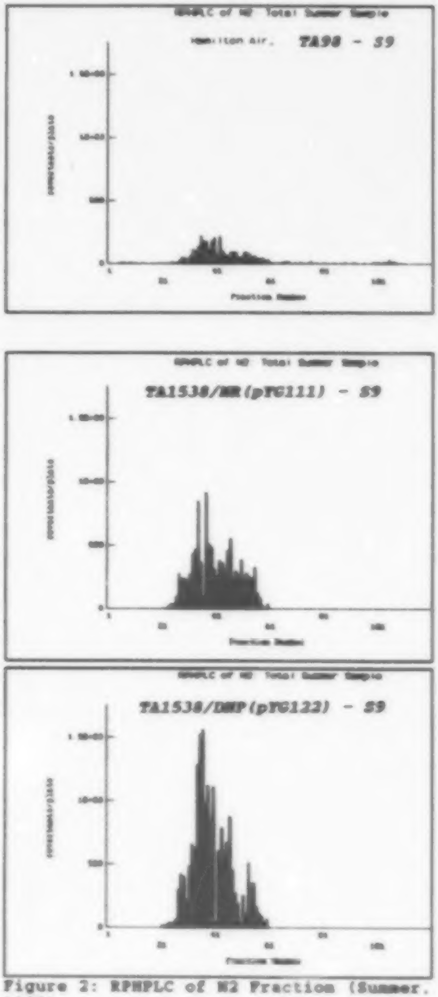

Figure 2: RPHPLC of N2 Fraction (Summer, 1988)

Table 4: MUTAGENIC RESPONSE OF THREE STRAINS TO (A45)
Revertants per cubic meter of air:

FRACTION	(pYG122)		(pYG111)		TA98	
	-S9	+S9	-S9	+S9	-S9	+S9
(A0)	1.49	3.57	1.17	3.07	0.55	0.93
(A1)	1.81	3.91	0.79	3.26	1.29	2.53
(A2)	0.16	0.15	0.41	0.52	0.26	0.21
(A3)	0.16	0.40	0.17	-0.15	0.23	0.12
TOTAL	3.61	8.03	2.54	6.67	2.32	3.78
MUTAGENIC YIELD (A45)(+S9):						
	4.83	9.30	3.91	6.63	2.00	3.88
PERCENT RECOVERY AFTER FRACTIONATION:						
	74.7	85.5	64.9	100.7	115.8	97.5

The examination of organic extracts of total suspended particulates collected over a protracted period is useful for the description of genotoxic hazards in general terms. A major goal of this study is to associate specific weather conditions and/or industrial activity with a potential impact on human health in Hamilton. For this purpose, we compared days when the wind direction was blowing from a sector extending from the north-east to east-south-east. This covers the area where industrial activity is concentrated in Hamilton.

We contrasted these days with samples of particulates collected during periods when the wind blew from south-east to west-north-west. Further matching of samples was done on the basis of NO_2, and ozone levels over the same three month period. As can be seen from Table 6, the atmospheric conditions which prevailed during the sampling period are reflected in the NO, SO_2, and COH average values. SO_2 was higher when the wind blew over the industrial area. This is expected since SO_2 generally indicates combustion emissions from stationary sources burning coal, heating oil, etc. The coefficient of haze (COH) as well as NO, both indicators of mobile as well as stationary sources, were elevated in these samples compared to those collected at the same location when the prevailing wind blew from the opposite direction. Carbon monoxide (CO) which is largely due to mobile emissions was similar for both sets of filters.

Table 6 examines the mutagenic activity of the samples based on the quantity of particulate deposited on the filters over the same period. Only the values for the most sensitive strain are shown. While particulate loadings were lower when the wind blew from the city toward the industrial area, the relative mutagenic burden per weight was much higher. Wind blowing from the industrial sector may contain a significant proportion of inorganic material (iron, sulfates, etc.) less likely to have associated PAH. Heavy vehicle traffic associated with the downtown location might contribute to the higher level of mutagens associated with urban particulates. The Main West sampler is sited near a highway exit (403) where one might expect substantial vehicle associated particulate deposition. The observed levels of mutagenicity at Main West, however, are essentially insensitive to wind direction.

Table 5: MUTAGENS IN AIR SAMPLES SELECTED FOR WIND DIRECTION AND LOCATION:
Correction to equal weights of particulate: TA1538/DNP(pYG122)

	ug/m³	rev/m³ in (pYG122)		rev/ug	
		A23	A45	A23	A45
(WITH S9 ACTIVATION)					
CIND	77	7.28	5.13	0.094	0.067
CURB	43	8.15	6.47	0.189*	0.150*
NWIND	49	5.31	3.42	0.108	0.070
NAMB	33	3.62	1.63	0.109	0.049
(WITHOUT S9 ACTIVATION)					
CIND	77	2.96	2.31	0.04	0.03
CURB	43	5.78	4.07	0.134*	0.095*
NWIND	49	2.76	1.78	0.05	0.03
NAMB	33	1.67	2.25	0.044	0.068

DNA ADDUCTS FROM URBAN AIR PARTICULATES:

Chemicals which form DNA adducts in target tissues are likely to be ultimate mutagens and potentially carcinogenic (Ashby, et al., 1989). We have begun a program to detect DNA adducts in bacterial tester systems with the intention of moving to primary cultures of mammalian target tracheal epithelium. Table 7 provides initial results of DNA adduct studies in Salmonella. The fractions tested include the most active [N] fractions of [A23]/LH20, and the total [A45] polar organic fraction. While initial results are promising, data are too few to support more than cursory analysis.

CONCLUSIONS:

The results presented confirm and extend previous findings. While the division of mutagenic activity into various fractions differs in detail from what was found for 1988. The inclusion of two additional bacterial strains has greatly increased the sensitivity of the bioassay system. These strains which possess increased ability to metabolise and activate nitro-PAH (pYG111) or PAH derivatives that are acetylated or activated to N-acetoxy intermediates (pYG122). TA98, relative to the other two strains consistently gives the weakest response to a given fraction. TA98, which carries the plasmid pKM101 is capable of a more sensitive genetic response than the other strains since it can convert DNA damage into mutations with a far greater efficiency than can the TA1538 strains. This is an indication that a significant portion of the detectable mutagens in atmospheric particulate samples could be nitro-PAH or their derivatives.

One of the major goals of this work is the characterization of an urban environment in terms of hazards posed by inhalable particulate. To approach this problem we have pooled selected groups of filters on the basis of similarity of prevailing atmospheric conditions during a collection period (Table 6). O_3, and CO were similar for all filters, but that NO, SO_2 and COH (coefficient of haze) were all higher for samples that represent conditions when prevailing winds blew industrial emissions over the city. SO_2 is mainly representative of stationary sources of fossil fuel combustion emissions, so its levels would be expected to rise under the sampling conditions. COH and NO are both indicators of mobile as well as stationary emissions.

Table 6: DNA ADDUCTS DETECTED BY POSTLABELLING IN TA1538/DNP(pYG122)

[N] FRACTIONS OF [A23]/LH20

	DIRECT	WITH 4% S9
[N1]		
500 m^3 AIR:	1.25 x 10^{-7} (2)*	1.6 x 10^{-7} (3)
1000 m^3 AIR:	2.89 x 10^{-7} (1)	1.3 x 10^{-7} (1)
[N2]		
500 m^3 AIR:	2.0 x 10^{-7} (3)	1.6 x 10^{-7} (3)
1000 m^3 AIR:	3.4 x 10^{-7} (1)	1.25 x 10^{-7} (1)
[N3]		
500 m^3 AIR:	1.15 x 10^{-7} (1)	1.3 x 10^{-7} (1)
1000 m^3 AIR:	2.6 x 10^{-7} (1)	2.3 x 10^{-7} (1)
[A45] (UNFRACTIONATED)		
500 m^3 AIR:	3.5 x 10^{-7} (2)	21.7 x 10^{-7} (2)
1,8-DINITROPYRENE (2.5 mM)		
	189 x 10^{-7} (2)	
DMSO CONTROL:	1.43 x 10^{-8} (4)	3.4 x 10^{-8} (4)

* The number of experiments to date.

When mutagenic activity was expressed as a function of weight of particulate deposited rather than volume of air sampled (Table 6) a clear difference between sample sets appeared. Particulates with the most potent mutagens were collected at the downtown location, and on days when the prevailing winds blew the industrial emissions away from the sampling locations. The most direct interpretation of this result is that mobile emissions and not industrial emissions seem to pose the greatest mutagenic potential. The particulates produced as a result of industrial activity in Hamilton (mainly associated with steel manufacture) contain considerable quantities of iron with lower levels of manganese, lead, chromium nickel, and cadmium as well as high levels of nitrates and sulfates (MOE Hamilton Air Quality, 1986). Thus, the lower mutagenicity per weight of particulate might be largely due to the much higher inorganic and bioassay-inert components that are characteristic of stationary emissions.

The apparent elevated levels of nitro-PAH detected by the bioassay system implicates NO and NO_2 as important actors in the genotoxicity of urban air particulates. Further chemical analysis will clarify which components of the atmospheric emissions provide the greatest concern for human health.

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A13

Eulerian Model Evaluation

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1.Introduction

Regional deposition models or Eulerian models as they have come to be called, represent an alternative means of predicting the effect of changes in emissions on deposition at a receptor point or region. Eulerian models take into account the complex homogeneous and heterogeneous atmospheric reactions which occur before the pollutants come to earth either in the form of precipitation or through deposition of gases and particulates. The regional models are more flexible than the mathematically simpler Lagrangian models in that they do not presuppose linear chemistry. Instead, by taking into account a non-constant scavenging rate as well as complex chemistry, Eulerian models can be used in situations where decreases in the emission rate at a source do not imply a constant proportional decrease at a receptor.

At present there are at least two principal Eulerian models of interest. They are: 1) the Acid Deposition and Oxidant Model (ADOM) developed at ERT under the sponsorship of the Ontario

Ministry of the Environment, the German Umweltbundesant, the Electric Power Research Institute and Environment Canada; and 2) the Regional Acid Deposition Model (RADM) developed for the Envrionmental Protection Agency in the United States. Before such models can be adcpted for assessing various emission control scenarios, it is necessary to evaluate them against observational data and more specifically to determine their margin of error. As well, it is essential that these models be scientifically credible and that predictions are made for the right reasons. In this project we address in part the issue of comparing model predictions with observational data. A key concern is that these are non-commensurable with respect to spatial scale. Models predict average deposition over a grid scale of 80 x 80 km^2 whereas observational data are point measurements which may be influenced by local variation and measurement error. As well, Eulerian models are capable of producing grid average hourly predictions whereas the monitoring networks produce measurements on variable time scales, daily, weekly or monthly. Models are not generally designed to predict fine-scale variability; instead, they usually predict regional scale patterns. Yet, they have in the past almost always been compared against point measurements.

3. The Approach

One of the goals of the present study is to recommend ways in which measurement data can be enhanced to make them more suitable for comparison against model predictions. Various sources of measurement data were considered. In particular, deposition data for sulfate, nitrate, cadmium and lead from the Major as well as the Ontario and Quebec networks were considered at various sites in Eastern North America for the Years 1985-86. As well, precipitation data from the Canadian Meteorological Centre (CMC) were obtained. Investigations were conducted to determine how precipitation data from CMC could be used to derive estimates of deposition.

A number of different estimates of deposition can be obtained using the available data. For simplicity, only annual estimates are discussed. For a single grid, let (C., P.) be the measurement of concentration of a pollutant and precipitation at the ith site. Assume that there are n sites within the grid in question. Then, the current estimate of deposition of the pollutant is given by

$$\overline{D_1} = \sum C_i P_i / n \qquad (1)$$

where the sum is taken over the n sites within the grid. Here n is usually small. A second estimate may be obtained by computing the average concentration and the average precipitation separately and then multiplying the two values as follows:

$$\overline{D_2} = \overline{C}\,\overline{P} \qquad (2)$$

A third estimate may be obtained by replacing the average precipitation in (2) which is obtained over sites by the average precipitation for CMC monitoring sites within the grid in question. The idea underlying the next estimate is that since CMC has a denser network of monitoring sites, incorporating these measurements into the estimate of deposition would tend to reduce the overall grid variability. Hence,

$$\overline{D_3} = \overline{C}\,\overline{P_M} \qquad (3)$$

where the subscript M indicates the average precipitation from CMC. Other estimates are of course possible. For example, precipitation may be estimated by interpolating precipitation over the entire Eastern North American region first. Then, the estimate for the grid in question would be used in (3). The quality of such estimates would be based on the assumptions inherent in the interpolation technique and are not discussed in this paper.

Given that an estimate of deposition is based on measurements of both concentration and precipitation, it is of interest to try to get a handle on the amount of amount of variation due to each. This was done for various grids with sufficient numbers of measurements.

3. Results

Annual sulfate, nitrate, lead and cadmium data were available for 1985-86 for Eastern North America. The region was subdivided into grids measuring approximately 100 x 100 km^2 . The number of sites within a grid varied considerably. Grids with two or more sites were used for the study of variability. It was observed that estimates (1) and (2) did not differ in any significant way; however, both of these estimates differ from (3) by as much as 25-30%, especially in the high deposition region in Southern Ontario. Sulfate and nitrate concentrations appear to vary less than site precipitation. This suggests in particular, the use of larger grid sizes might be reasonable for estimates of concentration. On the other hand, estimates of precipitation may require smaller grid sizes as could be provided from climatological networks. Further evidence was derived from a study of the respective variograms which measure variability throughout the Eastern North American region. A breakdown of the variability using estimate (3) as the standard indicates that approximately one third each of the variability can be attributed to bias, to concentration and to precipitation. This shows that improvement in the estimate of precipitation will likely lead to a significant improvement in the estimate of deposition. For cadmium and lead, the concentration varies considerably and improvements in the estimates of precipitation may have less impact. A comparison of site precipitation with precipitation from CMC reveals differences of as much as 25%. This points to a possible underestimation of deposition as calculated by estimate (1). Finally, results on the functional relationship of the variability in deposition to the mean were noted.

A14

TESTING ATMOSPHERIC DISPERSION MODEL PERFORMANCE

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ABSTRACT

Models of atmospheric dispersion of pollutants from elevated stacks are necessary to the development of effective pollution control strategies. It is essential that models used for this purpose be properly tested to ensure that they are reliable for the purpose intended and the conditions envisaged. Model validation, however, is difficult because of the dearth of suitable observational data sets against which model predictions can be compared. The Ontario Ministry of the Environment data set for the area around the smelters near Sudbury is therefore a valuable resource for this purpose. This paper describes the methodology and results of the use of this data set to validate two models of atmospheric dispersion. One was developed at Chalk River Nuclear Laboratories for the control of radioactive effluents to the atmosphere, the other was developed for the Ministry to be used in association with regulation 308.

INTRODUCTION

Being able to predict the temporal and spatial variability of atmospheric dispersivity is a necessary step in the development of effective air pollution abatement strategies. For steady sources the occasional whiff of pollutant concentrations well in excess of the long-term mean may be, and often is, the main cause of consequent harm or nuisance. Accidental, short- term releases of toxic substances can produce locally serious threats to the population. It is desirable to estimate the likely occurrence frequencies of such threats and the possible areas most likely to be affected.

Models to accomplish these and similar purposes should be capable of dealing with different source formats including different physical release heights and, where appropriate, different effective release heights because of excess buoyancy or momentum in the effluent gases. To be most useful they should be able to work with archived meteorological data from nearby synoptic weather stations.

Many codes, with which their proponents claim some or all of these tasks can be accomplished, are now in use. It is essential that the predictions be reliable enough for the proposed application and the limits of uncertainty associated with the model predictions known.

Model validation however is often difficult to obtain because of the paucity of suitable observational data sets. The measurements amassed by the Ontario Ministry of the Environment, consisting of the ground-level concentrations of SO_2 around 3 smelter stacks in the area of Sudbury, Ontario are, therefore, a most valuable resource for the testing of atmospheric dispersion models.

This paper describes the procedures we have followed using this data set to test 2 codes of atmospheric dispersivity. One of the 2 codes was developed at the Chalk River Nuclear Laboratories (CRNL) for use in controlling emissions of radioactive substances from nuclear installations. The other was developed in association with regulation 308 of the Ontario Ministry of the Environment (MOE).

OBSERVATIONAL DATA SET

The data set contains one-hour averaged ground-level air concentrations of SO_2 measured at 13 sampling sites deployed around the stacks (Table 1) in the years 1983/84. Monthly mean daily emission rates from each of the 3 stacks are also available for the same years.

Table 1. Distance between sampling sites and each site (km)

Site	Stack Height		
	381 m	194 m	93 m
77009	30.1	27.0	35.1
77010	31.3	32.3	13.2
77012	30.8	33.7	10.5
77013	21.1	24.9	13.6
77014	15.0	19.0	21.7
77016	3.8	6.8	18.1
77018	50.2	49.4	38.1
77028	15.8	16.6	10.5
77065	17.4	19.8	4.5
77066	92.2	94.7	70.6
77075	9.9	12.5	12.1
77096	8.6	5.1	24.8
77201	7.7	5.0	29.2

The three stacks have very different characteristics. Their heights vary from 381 m for the so-called "Super Stack" to 93 m for the shortest. The characteristics are summarized in Table 2. The relative positions of the stacks and sampling sites are shown in Figure 1.

Table 2. Source characteristics

	Height m	Stack Temp °K	Grid Velocity $m \cdot s^{-1}$	Emission Rate $g \cdot s^{-1}$
Super Stack	381	413	18.0	$1.93x10^4$
IORP	194	448	4.0	$1.81x10^4$
Falconbridge	93	413	6.5	$2.56x10^3$

THE MODELS

Both codes use a bi-variate Gaussian plume model formulation with dispersion parameters that are functions of atmospheric stability and distance. The CRNL code uses 6 stability classes while the MOE code uses 3. The two codes also differ in the manners by which the classes are identified. The CRNL code makes use either of the output of the STAR code (obtainable from the Atmospheric Environment Service of Environment

Canada) applied to the archived data from synoptic weather stations or from measurements of vertical air temperature profiles using an internal sub-routine based on a scheme described in IAEA (1980). The MOE code also uses archived weather observations from synoptic weather stations but determines stability classes using an internal routine. Differences also exist in the equations used to estimate horizontal and vertical dispersion parameters for each stability class. The CRNL code also uses archived climatological summaries in the form of occurrence frequencies of wind speed, directions and atmospheric stability.

More detailed descriptions of the two codes can be found in the reports listed in the bibliography.

For the validation tests here described the meteorological data sources were:

i) CRNL Code, CRNL-T. Hourly wind speeds and directions (10° intervals) and air temperature gradients measured at the Sudbury tower during 1983 and 1984. Wind characteristics were measured at 75 ft. (22.9 m) and the temperature gradient below 250 ft. (76.2 m). Stability class is determined using the scheme shown in Table 3.

ii) CRNL Code, CRNL-C. "STAR" output of stability class and wind speed and direction (22 1/2° intervals) from the AES synoptic weather station at Sudbury, Ontario.

iii) MOE Code. Hourly surface observations from Sudbury Airport and upper air soundings from Maniwaki and Moosonee.

Stability-class frequency distributions obtained by the two methods used by the CRNL code are shown in Figure 2. The IAEA scheme gives a much greater incidence of unstable conditions (classes A, B and C) and lesser incidence of neutral conditions (class D) compared to those from the STAR output. Similar differences were found when the IAEA scheme was applied to the CRNL tower data and STAR program was applied to the data from the nearby Petawawa A Weather Station (Barry and Robertson, 1986).

There were also significant differences in the wind directions in the two meteorology data sets (Figure 3) for example winds from 190° were 2 1/2 times more prevalent in the tower data compared to the climate data.

The codes were run with the appropriate input information to obtain:

1. The average of the hourly SO_2 concentrations predicted for each site in the years 1983 and 1984.
2. The cumulative occurrence frequencies of hourly averaged concentrations exceeding specified levels.

RESULTS

2-Year Average Concentrations: Ratios of predicted and observed average concentrations are shown in Table 4 and Figure 4. To obtain a symmetrical plot around the perfect result (ratio=1), the ratio is calculated with the larger concentration as numerator.

Table 3. Determination of the Stability Class from the Lapse Rate and Wind Speed

Lapse Rate LR	Wind Speed (m.s-1)					
(°K 100 m-1)	u<1	1<u<2	2<u<3	3<u<5	5<u<7	7<u
LR<-1.5	A	A	A	B	C	D
-1.4<LR<-1.2	A	B	B	B	C	D
-1.1<LR<-0.9	B	B	C	C	D	D
-0.8<LR<-0.7	C	C	D	D	D	D
-0.6<LR<0.00	D	D	D	D	D	D
0.1<LR<2.0	F	F	E	D	D	D
LR>2.0	F	F	E	E	E	D

Table 4. Ratios of mean predicted to mean observed concentrations (reciprocal if <1, denoted by -)

AVERAGE RATIO Cp/Co			
SITE	CRNL-T Cp/Co	CRNL-C Cp/Co	MOE Cp/Co
77009	-1.67	-2.50	1.32
77010	1.12	-1.63	-1.47
77012	-1.17	-1.83	1.66
77013	-2.16	-2.67	-2.20
77014	-1.30	-1.48	-1.74
77016	-1.02	-1.76	-2.92
77018	1.00	1.00	1.02
77028	1.28	1.13	2.40
77065	2.13	1.09	-1.54
77075	-1.10	-1.74	1.19
77066	1.30	-1.47	1.04
77096	1.19	1.28	1.01
77201	-1.11	-2.04	-2.49

The predicted 2 year-mean concentrations using the tower data in the CRNL area are, relative to those observed, marginally better than the other two. They also seem to be reasonably free of bias. Predictions based on the climatological data in the CRNL code are biased slightly low (about 30%). In both cases the predictions are within a factor close to 2. The MOE code shows a bias that is also slightly low but the predicted concentration for 3 of the 13 stations show discrepancies relative to the observed equal to or greater than 2.4.

Cumulative Frequencies: Cumulative frequency distributions of concentrations for three of the sampling stations are shown in Figure 5. They were chosen to show the range of results obtained. These results, typical of those from all the sampling sites, show that the CRNL code using Sudbury tower data gives frequencies which, for the most part, are within a factor of 3 of those observed (CRNL-T). When used with climatological data (CRNL-C), the predictions of the CRNL code are, on the whole, not so good.

This shows the loss of reliability in the predictions as the source of the meteorological information becomes less detailed and more remote. For example, the speeds and directions of the winds are measured at a height on the tower which is closer to the emission heights than those things measured at Sudbury airport. The wind directions cannot be resolved to better than 22 1/2° in the climatological data compared to 10° for the tower data.

The MOE code on the other hand grossly underestimates the lower concentrations and overestimates the larger ones. This is a feature seen at all sampling sites. The under- or overestimates are in many cases approaching factors of 10. The relatively good agreement between the 2-year average concentrations observed and predicted by this code appears then to have been, in part at least, fortuitous.

The CRNL code has also been used to estimate the contribution to the 2-year mean concentrations observed at each sampling site made by the individual sources. The results are shown in Table 5.

Table 5. Fraction of total concentration at each site due to each source

SITE	SOURCE STACK HEIGHT (m)		
	381 m	194 m	93 m
77009	0.41	0.21	0.38
77010	0.20	0.13	0.67
77012	0.20	0.11	0.68
77013	0.49	0.19	0.33
77014	0.37	0.21	0.43
77016	0.05	0.70	0.25
77018	0.31	0.16	0.54
77028	0.19	0.19	0.62
77065	0.21	0.11	0.68
77066	0.39	0.15	0.46
77075	0.39	0.31	0.31
77096	0.35	0.48	0.17
77201	0.24	0.56	0.20

SUMMARY AND CONCLUSIONS

The results of the present work have shown that concentrations of atmospheric pollutants in the region of known sources can be predicted by a relatively simply model (CRNL) and ready-to-hand meteorological data with sufficient reliability for many planning and regulatory applications. The MOE code, more complex and requiring additional meteorological input, does not perform quite so well against the particular observational data set used here. Nevertheless, it may prove, in the longer term, to be more flexible in its range of applicability than the simpler code.
It is important then to examine in detail the MOE code to find out which features have lead to the discrepancies noted here with a view to achieving an overall improvement in reliability. Comparisons between the outputs of the two codes under a variety of source and meteorological conditions should prove an effective tool in achieving this objective.

However, the discrepancies are relatively small and the potential effects of difference in the meteorological data inputs must be kept in mind. It is too easily assumed that defects in the predictions arise because of defects in the models whereas the limitations in model predictions may also arise because of imperfections in the input data. For example, the field samplers subtend an infinitely small angle at the source and an error in setting the anemometer in the grid system could cause substantial prediction errors at one small point in space. Wind directions known only to 22 1/2° sectors cannot give as good predictions as those known within, say, 5° intervals even with the same model.

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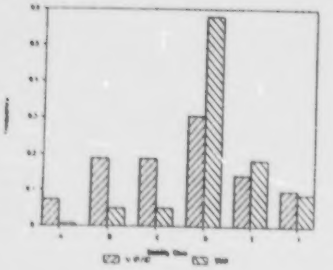

FIGURE 2. Frequencies of stability classes by schemes IAEA (1980) and STAR

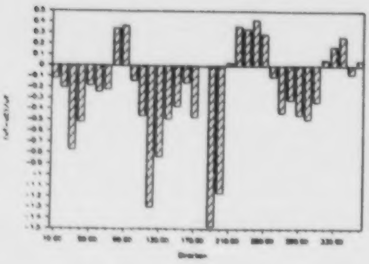

FIGURE 3. Relative differences between wind direction frequencies obtained from the Sudbury tower and the AES weather station at Sudbury airport

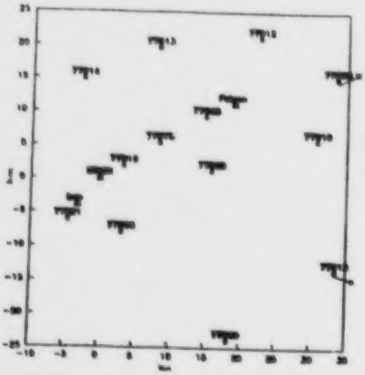

FIGURE 1. Relative siting of stacks and sampling sites

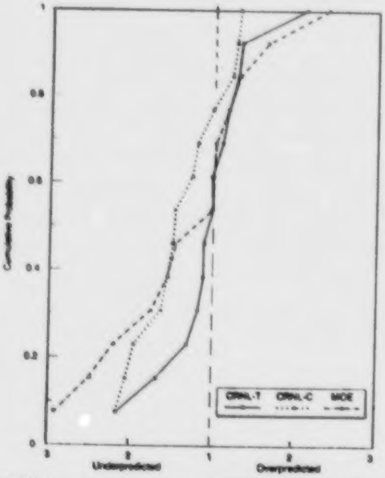

FIGURE 4. Frequencies of occurrences of ratios of 2 year mean SO_2 concentrations predicted and observed

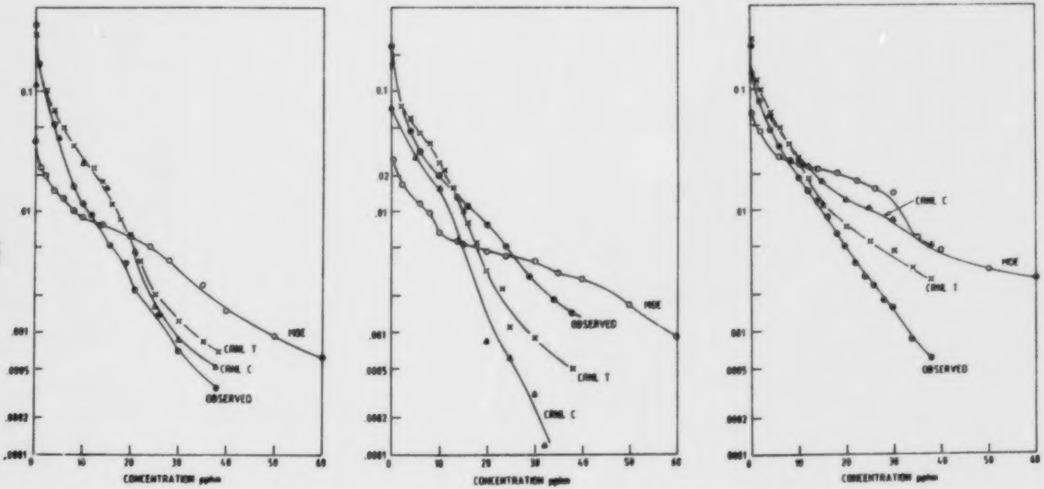

FIGURE 5. Cumulative frequency distributions of SO_2 concentration at three sites: 770016 (left), 770201 (centre), 770028 (right)

A15

SCALE MODEL STUDIES AND DEVELOPMENT OF PREDICTION PROCEDURES FOR HEAVY GAS DISPERSION IN COMPLEX TERRAIN

by

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ABSTRACT

Scale model experiments were performed to study the spreading of a heavy gas cloud in level terrain with obstacles. The cloud spreading rate was determined from video analysis. A cloud moving across terrain with a uniform array of obstacles started out initially as a circular cloud, and later a clearly defined diamond shape was observed. Cloud passage along the corridors was faster than without obstacles. Away from the corridors, passage was slower because of the higher resistance to flow. Accurate concentration profiles were measured with a high frequency flame ionization detector (FID). For validation purposes, the physical model predictions of concentration are compared with full scale releases performed at Thorney Island.

1. INTRODUCTION

The goal of this project is to develop a mathematical model which predicts the behaviour of a heavier-than-air gas cloud in an urban area. Current mathematical models apply to smooth terrain only, a significant limitation because spills are likely to have the most impact in suburban or urban settings. Several heavy gas experiments were performed at model scale in the RWDI wind tunnel at the Guelph facility. The setup, wind tunnel calibration, and preliminary testing were reported in Irwin et al. (1988). Testing is continuing with both uniform and non-uniform arrays of obstacles. Theoretical work is aimed at accounting for variation in the cloud movement between obstacles in uniform arrays. This paper summarizes the findings from both the theoretical and the experimental aspects of the project.

2. PHYSICAL MODELLING OF DENSE GAS RELEASES

Physical modelling consists of reproducing the behaviour of certain physical phenomena at model scale so that design parameters may be economically studied to determine their impact on the physical process of interest. In atmospheric modelling, a wind tunnel simulation of heavy gas dispersion is representative of a field trial if similarity is ensured for the following:

i) Reynolds number of the flow, $Re = D\ U\ \rho/\mu$
ii) Richardson number, $Ri = g\ L\ [(\ \rho_g - \rho_a)/\rho_a\ ]\ /\ U^2$
iii) density ratio, ρ_g/ρ_a
iv) volume and rate of release;

v) vertical wind velocity profile, U vs z;
vi) surface roughness, z_o;
vii) turbulence intensity; and
viii) length scale of turbulence.

Probably the most important parameter is the bulk Richardson number (Ri) which is based on the initial gas density and the approaching wind velocity. However, maintaining the same value of Ri at model and full scale often leads to a low wind velocity which goes against Reynolds similitude. In practice the density is often increased so that a higher velocity may be used while at the same time preserving a constant Ri. This approach was used in this work. Further details are available in Irwin et al. (1988). The release volume was scaled geometrically for instantaneous releases, and the vertical velocity profile was representative of Trial #13 at Thorney Island as described in McQuaid (1985). The runway and grass area surrounding the full scale releases were represented by a flat smooth surface. The turbulence intensity measured in the wind tunnel was slightly greater than the level observed at Thorney Island and the observed length scale was more representative of a 1:200 boundary layer than the expected 1:100. However, this was not expected to significantly alter the concentrations in the near field.

3. EXPERIMENTAL PROCEDURE

Instantaneous releases of heavy gas were conducted at both 1:100 and 1:50 model scales. The releases consisted of filling a circular cylinder with gas and dropping the sides to the floor. The spill event was recorded on video and gas concentrations were measured with a high frequency flame ionization detector. The released gas was a mixture of air and Freon 12, with mineral oil mist added to mark the cloud. The density of the release was measured to be 3.2 times the weight of air at room temperature.

Flow visualization studies were performed to obtain a detailed visual record of the impact of obstacles on the flow path of the cloud. Two sets of flow visualization data were obtained. The first set were taken in a test configuration located outside the wind tunnel in a calm or still-air condition. Releases were carried out over smooth flat terrain and on the same flat terrain but with obstacles.

A second set of flow visualizations were taken in the wind tunnel. The obstacle coverage downwind of the release extended twice as far as the coverage used in the calm wind tests. Releases were performed at model scale windspeeds of 0, 1 and 2 m/s over smooth flat terrain as well as over obstacles located on flat terrain.

Gas concentrations were measured with a new high-frequency Flame Ionization Detector. This fast response FID was developed for high speed sampling of combustion engines. Recently, the instrument has found application in gas dispersion research. The operating principle of the FID is chemionization and its high frequency capability is derived from the sensor being located in the head close to the source being measured. Depending primarily on sample tube length and sample flow rate, a response of up to 350 Hz is possible. In this work the response was measured to be on the order of 100 Hz.

4. FURTHER INVESTIGATIONS OF THE BOX MODEL IN STILL AIR

A photo study was presented in Irwin et al. (1988). From these series of photographs, the horizontal dimensions of the cloud could be determined and a time/distance history of the cloud front under a variety of release conditions ascertained.

Using a simple box model approach which assumes a cylindrical cloud of known dimensions (MOE, 1983), the gas slumping phase of a heavy gas release is controlled by gravitational effects. In this phase, the aerodynamic drag on the cloud ($\rho_a\ u^2\ C_D\ A$) is balanced by the net hydrostatic pressure head ($h\ g\ A\ [\rho-\rho_a]$):

$$\rho_a\ u^2\ C_D = h\ g\ (\rho-\rho_a) \tag{1}$$

where u is the frontal cloud speed, h is the height of the cloud, C_D is the aerodynamic drag coefficient, ρ is the density of the gas cloud, ρ_a is the density of air, and g is the gravitational acceleration constant. Assuming a constant cloud volume ($V_o = \pi h r^2$) during this phase gives the following relationship for the spread of the cloud under still air conditions:

$$r^2 = r_o^2 + 2Ct(gV_o d/\pi)^{1/2} \tag{2}$$

where r is the cloud radius at time t, r_o is the initial cloud radius, C is a constant related to the inverse of the drag coefficient, d is the ratio of the density excess of the heavy gas over ambient air to the ambient air density = $(\rho-\rho_a)/\rho_a$, and V_o is the initial cloud volume. It should be noted that (1) and (2) both refer to cloud spread in an unobstructing terrain only.

In last year's paper (Irwin et al., 1988), we reported on results of still air experiments which showed that the "best-fit" value for C ranged from 1.19 to 1.75 for the large canister (or 1:50 scale) releases depending on the obstacle configuration. Additional still air releases have been performed for block spacings of 21 cm (3:1 spacing) and 2 cm (0.3:1 spacing) with the 7 cm blocks which allows us to look more closely at the nature of the "constant" C.

Figure 1 shows the radius of the cloud as a function of time for the 1:50 scale release and a flow direction along the unobstructed corridor (90°). Close examination of the data indicates that the radius at any given time is generally least for the "no blocks" case and greatest for the 1:1 and 0.28:1 spacings with full coverage, and this difference increases with time. The model line in Figure 1 is a plot of (2) with C=1. With coverage of half the area by blocks ("half coverage"), systematic differences in the radii with respect to the "no blocks" case were not evident. It is evident, however, that the model with C=1 is not a good fit to the measurements after about 0.5 seconds.

Observations show that the rate of cloud spread may be related to the areal coverage of the blocks in the path of the gas cloud. Cloud movement for the full-coverage conditions down the obstruction-free corridor increases as the fraction of the area covered in blocks increases. Thus, for a given time, the cloud radius should increase with coverage in the following sequence: no blocks, 3:1 coverage, 1:1 coverage and 0.3:1 coverage. In order to explain the mechanism behind this behaviour, we recall that (1) was derived from the balance of the frontal drag on the cloud and the net hydrostatic head exerted by the cloud. The hydrostatic head is a function of the height of the cloud (h). Since we are assuming the volume of the cloud remains constant during this stage, the height decreases as the radius increases. This assumption allows us to derive (2) from the balance of forces. However, in the case of flow through obstructions (i.e. the blocks), the shape of the cloud alters from the cylindrical. Regardless of the shape which the cloud takes, once it begins to traverse the obstruction zone, the area of surface covered by the cloud will be reduced. The reduction will be the difference between the area which would be covered if the cloud base was circular, with a radius equal to the most distant point of advancement, and the sum of the base areas of the blocks. If R_x is the most distant point from the centre point of the cloud front, the potential area of surface coverage is πR_x^2. If the area covered by the obstructions is A_b, the actual area of the surface (A_w) covered by the cloud is $\pi Rx^2 - A_b$. Since we are still assuming constant volume, the height of the cloud (h) is V_o/A_w. From (1) we may determine the cloud frontal speed down the corridor to be

$$u = dR/dt = (h\ C\ g\ d)^{1/2} = (V_o\ C\ g\ d/A_w)^{1/2} \qquad (3)$$

Thus, the rate of spread is an inverse function of the surface area covered by the cloud base which decreases as the block coverage increases. The integration of (3) results in a complex relationship which cannot be solved for R directly. Since (2) can be made to fit the experimental data with a change in the value of C, an empirical solution was sought in which C is replaced by $C' \exp(\gamma t)$ where γ is an empirically determined term which is a function of block coverage and $C'=1.1$. Thus (2) becomes

$$r^2 = r_o^2 + 2C't(gV_o d/\pi)^{1/2} \exp(\gamma t) \qquad (4)$$

From the full coverage data, γ was found to be linearly related to the fractional coverage of the blocks (A_c). $\gamma = 0.11 + 0.56\ A_c$ where $A_c = s^2/(s^2 + l^2)$, s is the length of the block and l is the separation of the blocks. With half coverage, γ is approximately the same as for the "no blocks" case regardless of the degree of coverage on the block side. Figure 2 shows the new model versus experimental data for 3:1 and 1:1 block coverage.

For flow through the blocks, there is an inhibition of movement due to the presence of the blocks. Previously (Irwin et al. 1988), we defined a relationship for the distance of spread through the blocks (r_d) as $r_d = r\ f(t,\alpha)$ where $f(t,\alpha)$ was a function of time which depended upon the angle α from the corridor. With r expressed by (4) and $f(t,\alpha)$ by

$$f(t,\alpha) = \{(\Phi-1)\exp[-\beta t^2] + 1\}/\Phi$$

where β varies with block coverage and $\Phi = (1 + \tan\alpha)\cos\alpha$, the fit between model prediction and experimental data is good (for example, see Figure 3). Note that for $\alpha = 0$, (5) equals 1 and r_a reduces to r given by equation (4).

5. TEST RESULTS - CONCENTRATION FLUCTUATIONS

Model data are compared with Thorney Island Trial #13 in Figure 4. The ratio of measured downwind concentration to initial concentration in the release canister is plotted against the dimensionless time t^* (= t/t_o), where t_o is based on the initial release radius and potential velocity. Note, although the match between full and model scale parameters was not exact, the modelled concentration profile and peaks generally agree with full scale values, well within a factor of two. The cloud arrival time was somewhat longer in the model case, the difference between 20 and 30%. This is likely due to the difference in sensor heights.

The influence of obstacles on the cloud concentration is demonstrated by comparing Figures 5 and 6. Test conditions were identical except for the presence of the obstacles, and the sensor was positioned in the corridor 55 cm (55 m at full scale) downwind. At all windspeeds, the integrated area under the curves is larger with the obstacles in place. Also the peaks are similar in magnitude for all but the calm wind case. Thus, the dose-time relation has been increased with obstacles present. In other words, the gas concentration remains at a higher concentration longer with obstacles present than without. Closer scrutiny of Figure 4 (full scale) and Figure 6 (10 m/s) curves suggests that under high wind conditions, the cloud moving through the obstacles behaves similar to cloud behaviour with no obstacles present. Therefore, it is likely that above a certain windspeed the presence of obstacles makes little difference to cloud movement, unless the obstacles are very large.

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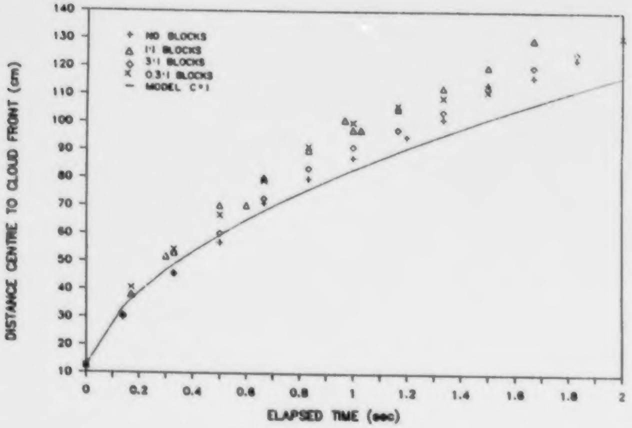

FIGURE 1

1:50 SCALE RELEASE – CLOUD FRONT FLOWING ALONG CORRIDOR

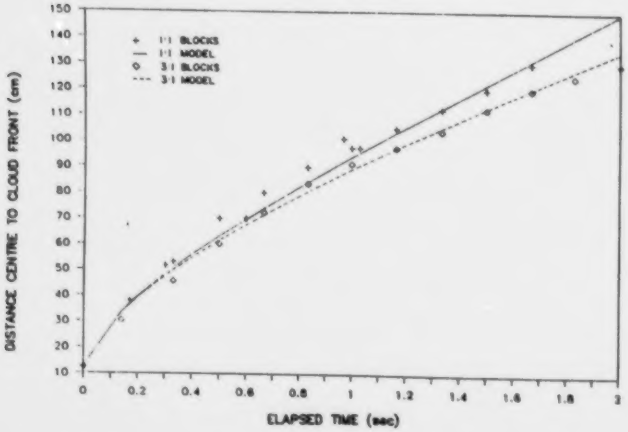

FIGURE 2

1:50 SCALE RELEASE – CLOUD FRONT FLOWING ALONG CORRIDOR

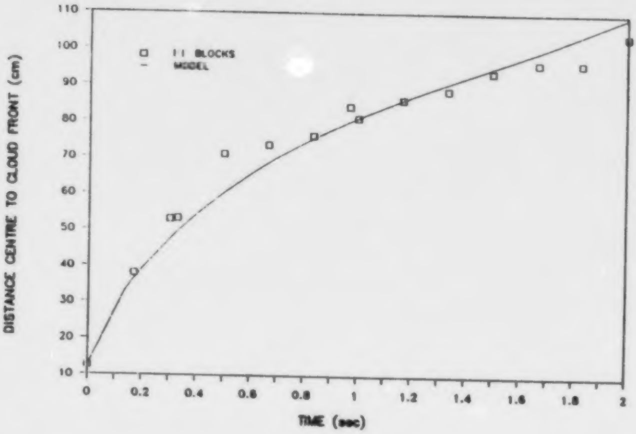

FIGURE 3

1:50 SCALE RELEASE - CLOUD FRONT FLOWING 45° FROM CORRIDOR

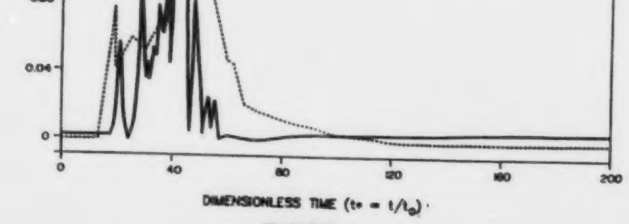

FIGURE 4

PHYSICAL MODEL COMPARED WITH FULL SCALE

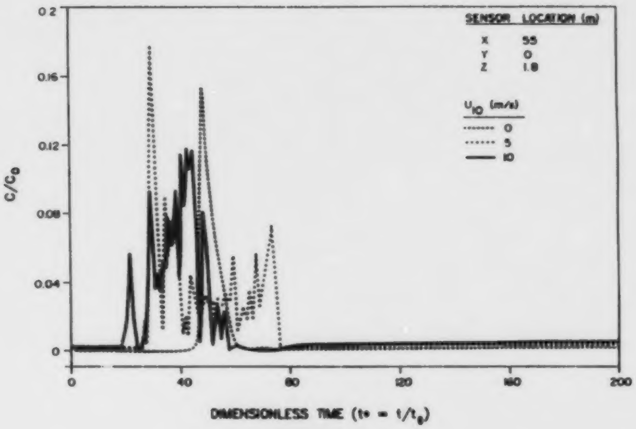

FIGURE 5

1:50 RELEASE - NO BLOCKS

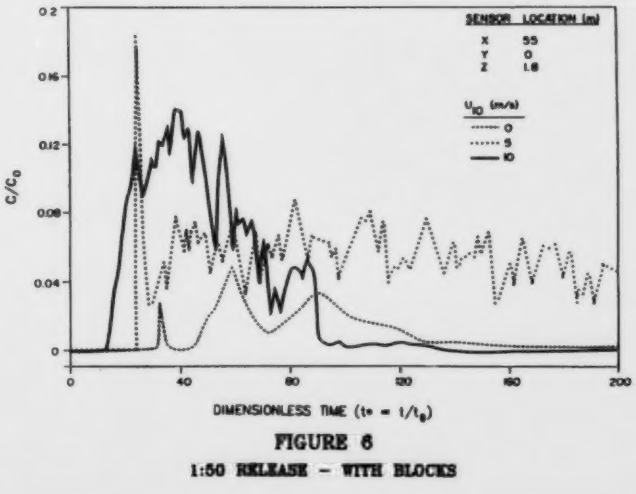

FIGURE 6

1:50 RELEASE - WITH BLOCKS

A16

Comparison of the Source Locations of Acidic Particles and Precipitation in Ontario

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Abstract

The potential source contribution function (PSCF) is a probability function based on the air parcel trajectory data couple with information regarding the nature of the contaminants measured in that air parcel. PSCF is the ratio of the probability of a contaminated air parcel having traversed a 1° latitude by 1° longitude area to the probability that any air parcel traversed that area. Regions with high PSCF values thus have a higher probability of contributing pollutants to the measured concentrations at the receptor site. Previously, PSCF analysis has been used on precipitation chemistry data obtained from the Acidic Precipitation in Ontario Study (APIOS) to locate the sources of the acidic precipitation. In this present study, the methodology has been applied to some particulate samples collected by APIOS network. The results of the analysis of the particulate data will be compared and contrasted with those from the precipitation study.

INTRODUCTION

Potential Source Contribution Function (PSCF) has been introduced to indicate the geographic areas that has high probability to be source areas of pollution events at a specific receptor site (Malm et al, 1986). The important feature of a PSCF analysis is the capability of geographically locating pollution sources whereas most commonly used receptor models (Hopke, 1985) identify pollution sources by their chemical characteristics rather than their locations. It is obvious that the locations of airborne pollutants are important information for air quality management. Previously, the PSCF method was applied to the study of acidic precipitation chemistry data sets obtained from Acidic Precipitation in Ontario Study (APIOS) network. These studies investigated the source locations of the precipitation constituents (Zeng and Hopke, 1989). In the present study, a PSCF analysis is applied to acidic species data in both precipitation and ambient particles collected by the APIOS network. The source locations of acidic species in precipitation and ambient particles will be compared.

METHOD

In the PSCF analysis, both sample chemistry data and related meteorological data are needed. From meteorological data, air parcel back trajectories ending at a receptor site can be calculated with a trajectory model (Olson et al, 1978; Bresch et al, 1984). Each trajectory consists of segments. A trajectory segment endpoint at certain time relative to starting time is calculated with a trajectory model (Olson et al, 1978; Bresch et al, 1984). Each trajectory consists of segments. A trajectory segment endpoint at certain time relative to starting time is given by longitude and latitude. To calculate PSCF, the whole geographic region covered by the trajectories is divided into many 1° longitude by 1° latitude cells so that PSCF will be a function of longitude and latitude coordinates. Let N represent the total number of trajectory segment endpoints during whole study period, T. If n_{ij} endpoints fall into the ij-th cell, the probability of this event, A_{ij}, is given by

$$P[A_{ij}] = \frac{n_{ij}}{N} \tag{1}$$

$P[A_{ij}]$ represents the residence time of a randomly selected air parcel on the ij-th cell relative to time period T. In same ij-th cell, if there are m_{ij} endpoints that correspond to the trajectories that arrived at a receptor site with pollutant concentrations higher than some pre-specified value, then the probability of this event, B_{ij}, is

$$P[B_{ij}] = \frac{m_{ij}}{N} \tag{2}$$

$P[B_{ij}]$ refers to the residence time for these contaminated air parcel. The potential source contribution function (PSCF) is then defined as a conditional probability:

$$PSCF = \frac{P[B_{ij}]}{P[A_{ij}]} = \frac{m_{ij}}{n_{ij}} \tag{3}$$

PSCF is the probability that an air mass with specified pollutant concentrations arrive at a receptor site after having been observed to reside in a specific geographical cell. Cells containing pollutant sources will have high conditional probabilities. Therefore, the conditional probability function, PSCF, will identify those source areas that have a potential to contribute to the high concentrations of contaminants observed at the receptor site (Malm et al. 1986).

DATA BASE

The chemistry data of daily ambient particulate samples and event precipitation samples are taken from APIOS network data base. Chan et al (1985) described this data base. Only the information related to this work is given here.

This study only focuses on acidic species at one site in the network, Dorset (station code 3011, see Figure 1). For precipitation samples from 1984 to 1986, the following four variables are considered: pH (PH), sulfate in mg SO_4^{2-}/l (SSO4UR), nitrate in mg N/l (NNO3UR), and ammonium in mg N/l (NNHTUR). Unreliable data were eliminated. A PSCF analysis can be separately calculated based on each of these variables. Before calculating PSCF, the original concentration data are converted to wet deposition of a species in a unit area by multiplying the concentration by the precipitation sample volume in ml (VOLUME). The purpose of this transformation is to eliminate the dilution effect caused by the differences in precipitation volume. The pH is converted to H^+ concentration, then to H^+ wet deposition.

For the ambient particulate samples, the species studied were sulfate in μg SO_4^{2-}/m^3 (SSO4FR), nitrate in μg N/m^3 (NNO3FR), ammonium in μg N/m^3 (NNHTFR), nitric acid in μg N/m^3 (NNRICF), and sulfur dioxide in μg SO_2/m^3 (SSO2FR).

Air parcel back trajectories ending at Dorset have been calculated by Ontario Ministry of the Environment (Olson et al. 1978). The trajectory data are provided in the form of a list of time intervals and coordinates of the trajectory segment endpoints for each trajectory. Trajectories using surface level data are calculated each day at 0:00, 6:00, 12:00, and 18:00 using 3 hour time intervals for 48 hours backward in time. In order to increase the resolution, a linear interpolation was performed to obtain 1 hour time interval trajectories.

RESULTS

Precipitation Data. By specifying samples with a deposition of a species higher than the average deposition of this species as polluted samples, the PSCF values can be calculated for each cell, and then plotted on the map. Figure 2-5 are the PSCF plots based on wet deposition of H^+, SO_4^{2-}, NO_3^-, and NH_4^+, respectively. Figure 2 shows that for high H^+ wet deposition events, the areas from Tennessee, Kentucky, and Indiana to the east coast are the source areas with PSCF > 0.4. Particularly, the Ohio River Valley region has PSCF higher than 0.6. A very similar pattern is observed in Figure 3, which is based on SO_4^{2-} wet deposition. The source areas of NO_3^- and NH_4^+ spread wider, especially towards the west to Missouri. The better relationship between H^+ and SO_4^{2-} than that between H^+ and NO_3^- or NH_4^+ suggests that SO_4^{2-} has greater effect on H^+ than NO_3^- or NH_4^+ has.

Ambient Particulate Data. The PSCF values can be calculated using average concentration as a cut-off value. Compared with SO_4^{2-} wet deposition (Figure 3), the source areas of particulate SO_4^{2-} (Figure 6) are similar in pattern, but much wider in size and higher in PSCF value. This result means that the whole midwest and east coast regions have very strong influence on the ambient SO_4^{2-} concentration at Dorset. Figure 7 and 8 show similar results except there are more high PSCF valued areas in the western of Illinois. This result is similar to the precipitation case, i.e. the source areas of N related species seems to spread more towards west. Figure 9 shows a extreme case of this group. In general, the whole region has much lower PSCF values for SO_2 (Figure 10) compared to SO_4^{2-} (Figure 6). SO_2 has much shorter residence time in the atmosphere so that it has less direct effect to a distant receptor (Dorset). Its effect is reflected by transformation to SO_4^{2-} in the process of transport.

Effect of Local Precipitation Events on Ambient Data. The ambient particulate samples can be split into two groups, one of them was collected during non-precipitation events, another was collected during precipitation event. Figure 11 and 12 are a pair of these results based on SO_4^{2-} particulate data. It was expected that the results were significantly different. However, the pattern of Figures 11 and 12 are very similar, and also similar to Figure 6. The similar results are obtained from other pairs. The results indicated that at least local precipitation events do not significantly affect the sources of particles in this size range. One possible reason is that these particles do not participate the precipitation formation process, and they are too small to be washed out by the precipitation.

CONCLUSION

With PSCF plots, pollution source locations can be easily identified in sense of conditional probabilities. The data sets used in this study consist of four to fourteen hundred samples. Therefore, the results are statistically significant. The PSCF plots indicate the U.S. midwest and east coast as source areas for most acidic species, both in precipitation and in ambient particles, at Dorset, Ontario, Canada. There are little differences between precipitation and ambient particles in terms of source locations, but the influence of these areas is stronger on ambient particles than on precipitation. The effect of local precipitation on the source locations of ambient particles is not significant. The results do not show the Sudbury as a source area.

This work was supported by the Ontario Ministry of the Environment under Grant No. 697.

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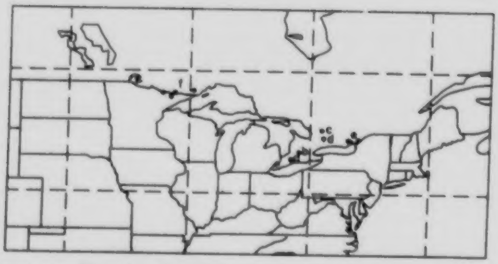

Fig. 1. APIOS Event Wet/Dry Deposition Network Station Location Map. (a) Stations 1011 and 1021; (b) stations 1031 and 2011; (c) stations 3011 and 3021; (d) stations 3031 and 3041; (e) stations 4011, 4021, 4031, and 4041; (f) stations 6051, 6061, 6071, and 6081.

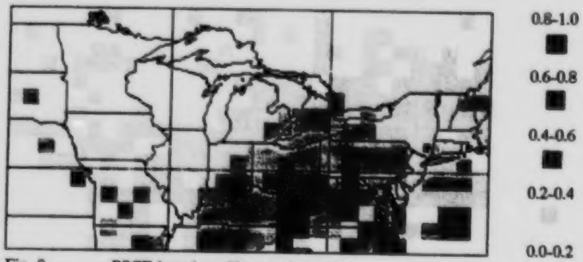
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 2. PSCF based on H⁺ wet deposition.

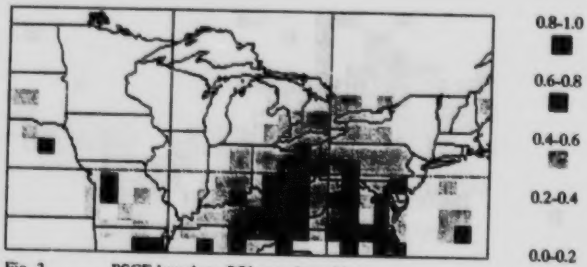
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 3. PSCF based on SO_4^{2-} wet deposition.

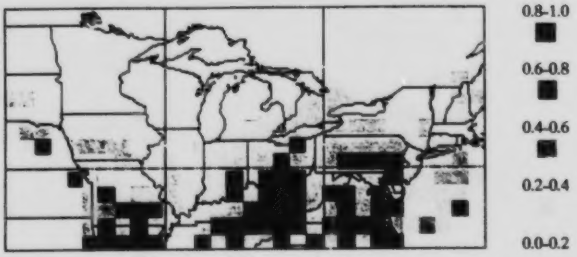
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 4. PSCF based on NO_3^- wet deposition.

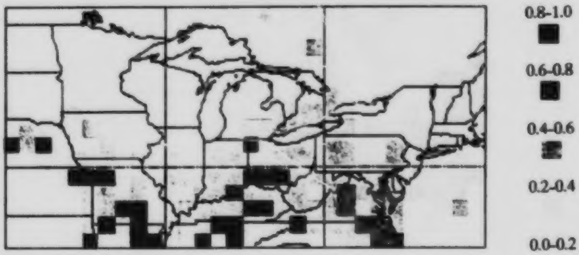
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 5. PSCF based on NH_4^+ wet deposition.

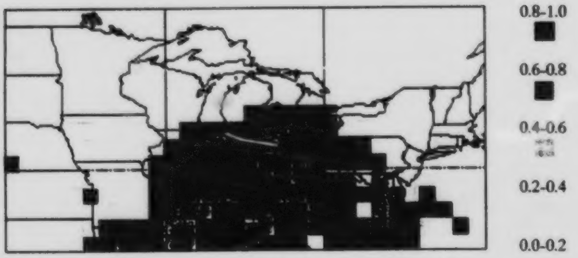
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 6. PSCF based on ambient SO_4^{2-} concentration.

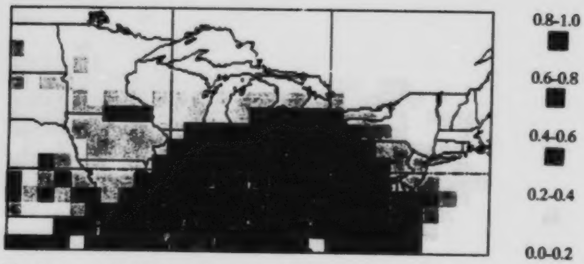
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 7. PSCF based on ambient NH_4^+ concentration.

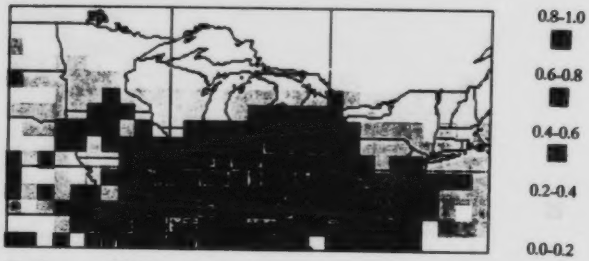
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 8. PSCF based on ambient HNO_3 concentration.

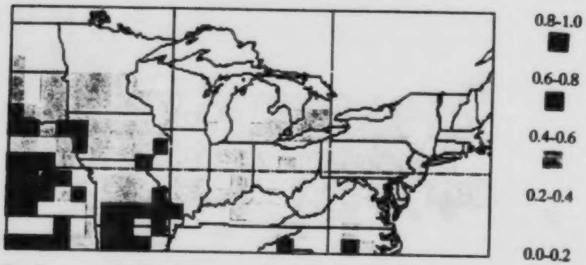
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 9. PSCF based on ambient NO_3^- concentration.

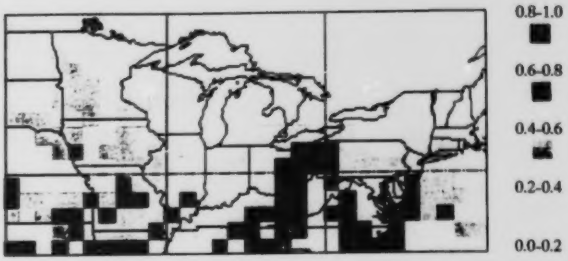
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 10. PSCF based on ambient SO_2 concentration.

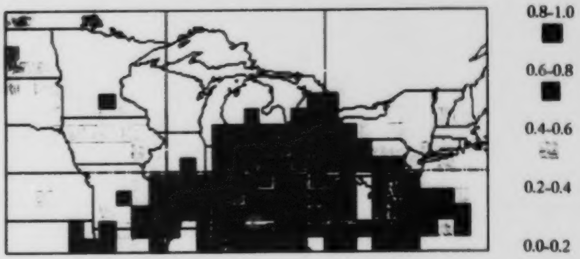
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 11. PSCF based on ambient $SO_4^=$ concentration during precipitation events.

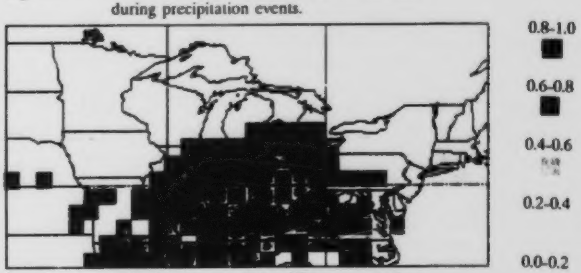
0.8-1.0
0.6-0.8
0.4-0.6
0.2-0.4
0.0-0.2

Fig. 12. PSCF based on ambient $SO_4^=$ concentration during non-precipitation events.

A17

IMPACT OF OZONE EXPOSURE ON VEGETATION IN ONTARIO

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This report summarizes the results of extensive efforts which have been undertaken in Ontario to assess the impact of ozone and other oxidants on all types of terrestrial vegetation and to provide a scientific basis for the derivation of economic benefits which would result from an ozone control program (Pearson, 1989 and Donnan, 1989). Other objectives were to assess the response of vegetation to other regional pollutants, to multiple pollutant exposures and to determine the ozone exposure threshold which would be required to virtually eliminate adverse impacts on crops, ornamentals and forests in the province.

In the case of agricultural crops, the derivation of production losses was accomplished by a thorough review of the scientific literature as well as many un-published government and university reports and conference proceedings and the development of a database for crop response to seasonal mean ozone concentrations of 40 and 50 ppb. A total of 19 crops were assessed in this manner, and for 12 of the 19, a comprehensive adjustment factor approach was utilized in the estimation of crop loss in Ontario due to ozone to compensate for geographic, agronomic and experimental variability in the research results. Based on these findings (Table 1) and an analysis of the Ontario ozone database (Table 2) in which minimum, maximum and average contours of seven-hour seasonal means were contoured via a kriging technique (Figure 1 - average), it was subsequently determined by Donnan (1989) that the annual value of increased crop production in Ontario would average $39 million, ranging from $14 to $61 million per year (Table 3). These estimates, which are expressed in 1986-87 dollars, assume that no added costs of cultivation or harvesting would be incurred. A statistical analysis of the Ontario ozone database from a seasonal average and hourly basis revealed that attainment of the existing one hour ambient air criterion of 80 ppb (Figure 2) would result in seasonal mean ozone levels below 40 ppb, thereby virtually eliminating productivity type impacts on seasonally exposed ozone sensitive vegetation in the province.

In the case of ornamentals, including landscape trees, turfgrass and Christmas trees, productivity losses were estimated at an average of 5% with a range of 2-7% in the southern portion of the province exposed to seasonal mean ozone concentrations at or above 40 (Figure 1). The value of the potential increased revenues to ornamental plant growers, if ozone levels were reduced to below 40 ppb (seasonal mean averages), has been estimated by Donnan (1989) to range between $2 and $8 million per year (Table 3)

Although foliar injuries have been documented on many forest species in Ontario, the state of knowledge at this time was insufficient to develop a reliable estimate of productivity losses. However, it has been noted (Pearson, 1989) that in Ontario, the major portion of the forest industry is located in an area of the province where ozone levels normally are lower than in the agricultural production areas of southern and central Ontario.

An evaluation of the impacts of other oxidants, including peroxyacetyl nitrate (PAN) and nitrogen dioxide failed to indicate any concern for direct impacts on vegetation at existing air quality levels. However, interactions involving these oxidants with ozone can not be ruled out due to a dearth of research conducted under growing season, field conditions. In the case of multiple exposures involving ozone and sulphur dioxide or acid rain/fog, there has been field type research that appears to rule out any significant enhancement of crop productivity losses. In the case of trees, the role of pollutant interactions which have been documented under controlled experimental conditions has not been clarified under natural or stand conditions.

In summation, this investigation documented productivity losses to crops and ornamental growers due to prevailing ozone concentrations. If ozone levels were reduced to a seasonal mean below 40 ppb, the value of the extra crop production and revenues to ornamental plant growers could range from $17 to $70 million, depending on the seasonal precursor emissions and the regional weather patterns for southern Ontario. These estimates can be compared to estimates of the costs of reducing ozone precursor pollutants from stationary and mobile sources in Ontario which are being prepared as part of an oxidant strategy for the province.

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Figure 2

STATISTICAL RELATIONSHIP: MAXIMUM HOURLY AND SEASONAL MEAN O3

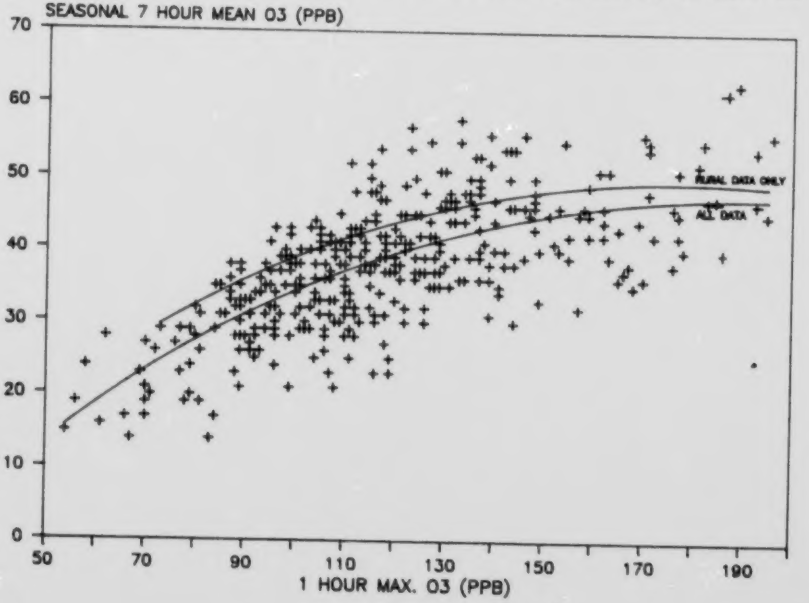

FIGURE 1 CONTOURS OF AVERAGE SEASONAL 7 HOUR MEAN OZONE CONCENTRATIONS IN ONTARIO : 1974-88

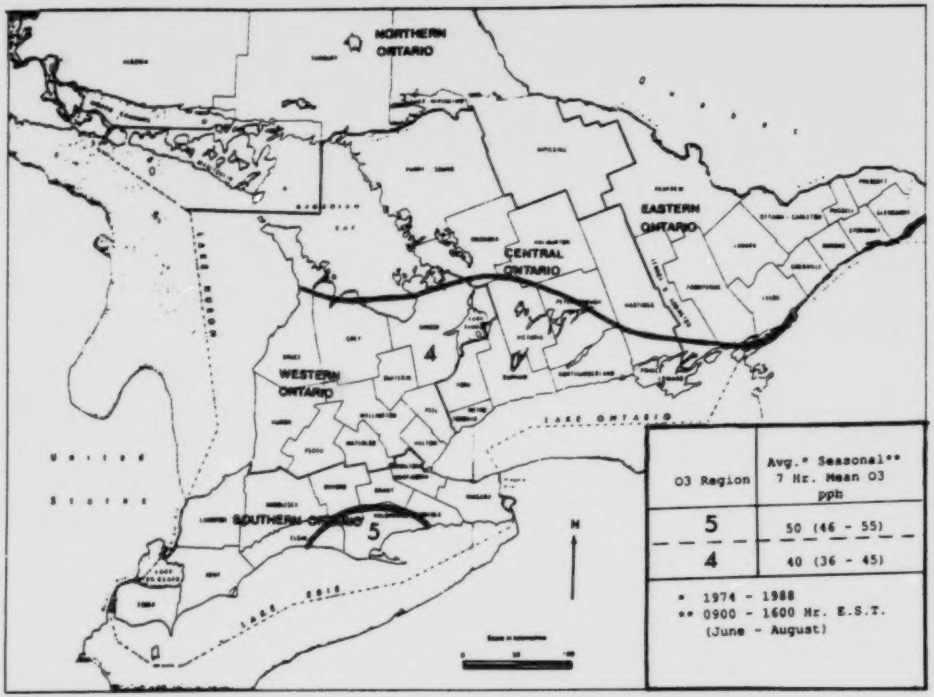
NORTHERN ONTARIO
EASTERN ONTARIO
CENTRAL ONTARIO
WESTERN ONTARIO
SOUTHERN ONTARIO
LAKE HURON
LAKE ONTARIO
LAKE ERIE
United States
4
5
N
O3 Region
Avg.* Seasonal** 7 Hr. Mean O3 ppb
5
50 (46 - 55)
4
40 (36 - 45)
* 1974 - 1988
** 0900 - 1600 Hr. E.S.T. (June - August)

Table 1

SUMMARY OF ESTIMATED CROP LOSS DUE TO OZONE EXPOSURE IN ONTARIO

CROP	AVERAGE YIELD LOSS IN ONTARIO -	
	OZONE REGION 4	OZONE REGION 5
AT RISK		
Dry Beans	10.6	10.7
Potato	5.6	6.9
Onion	5.6	9.2
Hay	4.4	4.3
Turnip/Rutabagas	3.8	7.4
Winter Wheat	3.4	5.5
Soybean	3.2	6.2
Spinach	2.5	4.7
Green/Snap Bean	2.2	4.4
Flue-cured Tobac	2.1	3.9
Tomato	1.6	5.4
Sweet Corn	1.4	2.3
MARGINALLY AT RISK		
Cucumber	1	2
Squash	1	2
Pumpkin	1	2
Melon	1	2
Grapes	1	2
Burley Tobacco	1	2
Beet	1	2

Table 2

SUMMARY OF OZONE CONCENTRATIONS (ppb) AT SELECTED RURAL AND URBAN LOCATIONS IN SOUTHERN ONTARIO: 1988 VS 1974-88

LOCATION	NO. YRS. MONITORED (1974-88)	URBAN/ RURAL	MAX.* 1 HR O3		7 HR SEASONAL MEAN** O3		NO HOURS**** O3 >					
				AVG.*** (RANGE)		AVG.*** (RANGE)	80 ppb		100 ppb		120 ppb	
								AVG.*** (RANGE)		AVG.*** (RANGE)		AVG.*** (RANGE)
			1988	1974-88	1988	1976-88	1988	1974-88	1988	1974-88	1988	1974-88
WINDSOR	15	U	188	148 (104 - 274)	62	45 (34 - 62)	173	61 (12 - 173)	68	18 (1 - 68)	26	5 (0 - 26)
MERLIN	10	R	133	112 (87 - 137)	58	42 (28 - 58)	173	35 (1 - 173)	45	7 (0 - 45)	8	1 (0 - 8)
LONDON	14	U	137	117 (99 - 166)	53	42 (36 - 53)	95	30 (5 - 95)	28	6 (0 - 38)	4	1 (0 - 8)
CENTRALIA	12	R	127	120 (100 - 137)	55	44 (35 - 55)	114	39 (8 - 114)	28	6 (0 - 28)	3	1 (0 - 3)
SIMCOE	14	R	196	129 (99 - 196)	56	51 (43 - 56)	109	54 (20 - 113)	41	12 (0 - 41)	5	2 (0 - 12)
TORONTO &	15	U	158	133 (86 - 201)	42	39 (28 - 60)	71	44 (5 - 162)	20	13 (0 - 98)	5	5 (0 - 49)
STOUFFVILLE	15	R	161	145 (84 - 312)	51	43 (29 - 67)	88	44 (1 - 181)	21	16 (0 - 97)	8	8 (0 - 68)
DORSET	7	R	195	107 (80 - 195)	45	37 (32 - 45)	64	16 (0 - 64)	6	1 (0 - 6)	0	0 (0)
SUDBURY	13	U	84	90 (70 - 118)	36	24 (14 - 36)	0	1 (0 - 3)	0	<1 (0 - 1)	0	0 (0)
OTTAWA	12	U	127	95 (76 - 127)	35	31 (27 - 39)	20	6 (0 - 24)	3	<1 (0 - 3)	0	0 (0)

& SITE AT DOWNTOWN TORONTO LOCATION (BREADLEBANE)

* MAXIMUM 1 HOUR CONCENTRATION (JAN - DEC: 0000-2400 EST)

** JUNE - AUGUST FROM 0900 - 1600 EST (7 HOURS PER DAY)

*** AVERAGE OF ALL YEARS MONITORED

**** DURING PERIOD OF JUNE - AUGUST FROM 0900 - 1600 EST

TABLE 3

VALUE OF PRODUCTION INCREASES FOR AGRICULTURAL AND ORNAMENTAL CROPS FROM OZONE CONTROL

VEGETATION TYPE	POTENTIAL MINIMUM	PRODUCTION MEAN	INCREASE MAXIMUM
		($ IN MILLIONS)	
AGRICULTURAL CROPS	14.4	38.8	61.4
ORNAMENTALS	2.2	5.7	8.2
TOTAL	16.6	44.5	69.6

A18

CARBOHYDRATE AND MICRONUTRIENT PROFILE OF SAP IN HEALTHY AND DECLINING SUGAR MAPLE TREES IN ONTARIO

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INTRODUCTION

A systemic information about the sap chemical composition of sugar maple trees, both healthy and declining, is not available in the literature and is not covered by other studies in ths field of sugar maple decline research. It is expected that if environmental factors have interfered with the biological processes of a normal maple tree then it would react with the biological and physiological composition of xylem sap carbohydrates, micronutrients and trace elements. The latter would perhaps be reflectd in the major chemical components of the xylem sap and stem tissue. Five sample plots, previously established by OMOE as part of its Hardwood Decline Survey Project in 1986, were chosen for site studies. Early (March) and late (April) season sap samples were collected aseptically from these sites in 1988 and from two of these sites in 1989. Micro-, macro-elements and trace metals are analysed by AA and ICAP Spectroscopic methods. Mono-, di-, and oligo-saccharides in the sap were investigated by High Pressure Ion Exchange Chromatography (Dionex Corp., Sunnyvale, California). This method of sugar analyses offered a very high resolution (30-100 ppb) for quantitative chemical determination. The method was standardized in our laboratory and provides highly reproducible results. This method has eliminated the uncertainties associated with other existing methods of carbohydrate determination. To provide secondary support for the carbohydrate determination, various other biochemical parameters for example, pH, dry weight, refractive indices and optical isomerism of the samples have been recorded for gross estimation. Compilation of data of all these response variables might provide indication of biological disturbances and corresponding chemical changes taking place in declining maple trees when compared with healthy trees. Work on stem and soil matrices of these trees is also underway as a part of a separate study.

We had earlier proposed that at the present stage of our scant knowledge of sugar maple decline, a useful approach might be to study the chemical changes occurring in sap in trees ranging from healthy to seriously in decline. The long-term objective being that if we could index the chemical change in xylem sap of declining maple trees, relationships could then be correlated with a physical assessment criterion, Decline Index (DI), recently formulated by OMOE and is currently being used in many related studies. It might further be possible to index these trees chemically much earlier than the onset of the physical decline, thereby facilitating the "early warning" syndrome of maple decline. The focus of this research, therefore lies in chemical analyses of xylem sap. To the best of our knowledge, this scientific study has not yet been pursued by any other research group involved in sugar maple decline research.

EXPERIMENTAL DESIGN

The sampling unit of this study is an individual healthy and declining tree of any of the five sites selected in a NE to SW directional gradient of southern Ontario. Ten sugar maple trees, differeing in physical health (as determined by OMOE's DI) and site characteristics (mainly pedological and stand) are selected each from five sites varying in their overall decline status. These sites were mapped out in 1986 as part of the Hardwood Decline Survey, conducted by MOE.

One of these sites has been demarcated as a "base-line site" , which will provide a statistically acceptable pattern of variability in levels of sap chemicals. Fifty trees at various stages of decline have been marked for study at this site. This site will further provide data to study the extent of intra-site variability in these trees. All sites selected have been unmanaged for at least past 17 years, contain at least 50% sugar maple trees, and are situated on the Crown Land, basically undisturbed by any human interference. The crossed factorial design of this study includes five sites. Trees were selected so that the healthy trees have DI of <10.00 and declining trees are branded DI of >10 and LE 90. The trees in each site varied in decline from less than 10 to 100 (as established by McLaughlin et al. 1988). For convenience of handling data in our laboratory, we labelled the trees in different categories. In sites 61, 62, 45, and 73, where we sampled only 10 trees each (5 healthy, 5 declining), the trees were coded H if the decline was less than 10. Trees with decline of greater than 30 and less than 90 were coded D.

H = decline <10
D = decline >30 and <90

In site 20 the tree coding spanned a range of DIs, as elaborated below:

A = healthy trees, decline <10
B = decline 10 - 30
C = decline 31 - 60
D = decline 61 - 90

Within each category, an attemp. was made to include some dominant and some suppressed trees to study the nature and effect of the stand competition on decline.

The general trend analyses were performed on the basis of these decline categories rather than on the individual numerical values of the physical decline.

Xylem sap at breast heights (1.3 meters) of selected trees have been collected at both early and late sap flow seasons in March and April months of 1988, respectively. Stem tissues were collected in early Fall of 1988 along with the soil samples from the rooting zone along the drip line of each tree. At the time of stem and soil collection, the decline status was assessed with the physical parameters set forth by OMOE.

The major response variables selected for the sap study are Sucrose, Glucose, Fructose, Galactose, Raffinose, xylose and Arabinose. The major inorganic elements selected are:

Macronutrients (Na, K, P, Ca, S, and Mg)
Micronutrients (B, Cu, Fe, Mn, Zn)
Other elements (Al, Co, Cd, N, Pb, Si, Cr, As, Se, Sb,
V, Mo, Ni, and Ba)

SAP COLLECTION

For sap collection, aseptic conditions were used to avoid metal contamination which might interfere with the trace elemental analyses. A custom designed polyethylene plastic suction apparatus was designed for the extraction of xylem sap in maple trees in the field by MOE (McLaughlin 1987). This apparatus was used for the extraction of sap samples in these sites. A two inch size of hole was drilled by an automatic drill attached onto a chain saw at the south side of the breast height of the trees. A maximum pressure of 120 psi, applied by hand-held lysimeter pump, was enough to yield sufficient amount of sap (30-100) from each tree in 5-20 minutes. As mentioned in the abstract all 90 trees were tapped for sap samples twice during the sap season of 1988 and during 1989, four sap samples were taken from the ten trees of site 45 at a weakly interval and two samples each from ten trees of site 73 were taken at early and late season, respectively.
In 1988, a total of 180 sap samples were collected (90 early sap season samples and 90 late season samples from 90 trees). In 1989, 60 more samples were collected (10 each week from site 45 trees for four weeks and 10 early and late samples from site A073 tres). The total volume of collected samples varied between 25-100 mL. Each extracted sap sample was aliquoted and distributed equally in 4 sterile plastic vials (30 mL. capacity). The samples were kept cold in the field and frozen at -15°C as soon as possible. The frozen samples were thawed and diluted with deionized water (10-

1000 X) prior to analyses.

ANALYTICAL PROCEDURES

Simple sugars and di- and oligo-saccharides were analysed by High Pressure Liquid Ion Exchange Chromatography (HPLIC), a new technique marketed recently by Dionex Corporation (Sunnyvale, California), as BioLC Series 4000i. Carbohydrate standards, including some ultrapure carbohydrates, obtained from Pfanstiehl Lab. Inc., Illinois, USA, were used for statdardizing the HPLIC chromatograms. All these carbohydrtaes with a detection limit as low as 30 ppb for monosaccharides and 100 ppb for polysaccharides can be separated as anions with a concentration elution gradient program of sodium hydroxide. Retention times and selectivity of the analytes are easily controlled by varying eluent strength. The separated carbohydrates were detected electrochemically by oxidation of a gold electrode. This potent method of direct separation of carbohydrates offered a timely option to replace other cumbersome and unreliable analytical methods (e.g. HPLC utilizing RI and low UV-detection and GC after derivitization of samples) of carbohydrate analyses. These latter methods were tried earlier to establish the ideal conditions for sap samples with limited success. On the other hand, we have found the Ion Exchange Chromatography to be sensitive (30-100 ppb), linear (upto 600 ppm concentration), reproducible (peak heights vary less than 1% after multiple injections of single sample) and in control of retention at both isocratic and gradient elutions of a sample.

After standardizing the system for representative sugars, carbohydrates were analysed in the sap samples. Figure 6 shows a chromatogram of six carbohydrate when eluted in a concentration gradient program of NaOH. A computer program in Basic language was developed to calculate the concentrations of known sugars. The method was based on the absolute normalization criterion. An ID profile was developed to calculate the response factors of the known sugar standards and these were used to analyse the field sap samples.

OBSERVATIONS

An extensive survey of literature revealed that no systematic information is available regarding the chemical composition. It is apparent that there is a problem of actually identifying what the chemical compositions of normal sap and syrup samples should be. Since our studies incorporate a detailed analysis of carbohydrates, which these older studies do not provide, a relative comparison of the chemical composition of healthy and declining trees is emphasized than pinpointing as to what is normal and what is not normal. Our objective has been to explore the presence of the abnormal sugars and defining the processes which could be triggering this abnormality. This could have a bearing on the stattus of health of maple trees. The process(es) leading to these abnormalities could offer us a predictor capabilities if we assume that everything other than the health of the trees is constant.

The pH distribution of sap samples collected in early and late season of 1988 was studied in healthy and declining trees in each site. It appears that in general, the pH of the late sap samples were lower than those of early samples and the pH was distinctly lower in declining trees of sites other than site 20.

The amount of total solids present in sap was measured by Abbe's refractometer. The percentage distribution of solids differed in early and late samples. A similar decreasing trend in the presence of dry weight was found when a unit volume of sp lyophilized gravimetrically to determine the sap dry weight. The volume of sap collected per tree differed when standardized to a unit amount of time (15 minutes with or without the help of lysimeter pump suction). Consistently, lesser amount of sap was colloected in declining trees and any tree during late season from each site. When the volume of sap collected was normalized to the total dry weight measured to estimate the amount of sap in each tree, we noticed a decreasing trend.

There are distinct differences in carbohydrate contents of early and late season sap samples and the samples taken from healthy and declining trees, irrespective of the season. The trends of changes seems to be similar in the two groups: healthy trees resemble the trends similar to the early samples and late samples that of declining trees. For example, late samples have less total sugars than the early ones, there is more sucrose in early than late samples and healthy versus declining trees. Healthy trees have less of smaller unknown peaks than the declining trees and the extent of smaller sugars e.g. arabinose and galactose increases in proportion compared to those of healthy trees. More invert sugars in declining trees and late samples. Furthermore, these changes seem to be present in all the late season samples and all the declining trees, no matter which site the samples were coming from. Therefore these changes seem to be unaffected by the location and pedology or other characteristics of the site.

Estimation of the total Nitrogen content of the sap samples was attempted by Kjeldahl's method with the hope that the total protein content of corresponding sap samples will be calculated from these data. The nitrogen content was found to be below the detection limits of this procedure. In this event since the protein content is too low to be analyzed by Kjeldahl's method, an alternative microanalytical method will be investigated to determine nitrogen (and protein) content.

For inorganic chemical determination of elements other than N, Na and K, we used ICAP method. A random survey of 10 samples for Ca, Mg and Mn determination by both methods showed that the concentrations determined were similar. This made us feel comfortable in reporting the ICAP elemental onservations since many laboratories still analyse elemental data by AA. The 27 elements were anlaysed by ICAP in both early and late sap samples. Lyophilized sap samples were prepared in ultra-pure 6% nitric acid matrix and analysed in ICP laboratory at the U.of Toronto. The preliminary observations of the data revealed a decreasing trend of CA, K, B and an increasing trend of Al, Mn, Fe, Na, and Ba in declining trees. Site 20 trees showed a range of these trends with respect to the decline indices. Mg and Ca seems to be showing an unusual antagonism which needs to be investigated further. Site 73 appears to have an increased level of Al and Ca than other sites. The levels of other elements like Mo, Ni, Pd, Co, S, P, As, were not significantly different in these trees both in early and late season samples. Levels of Co, Cr, Cd, V and Sb were found to be near zero.

The data so far analysed and described here are in terms of the average trends only. We are in the process of carrrying out the statistical analyses to mesaure intra- and inter-site variabilities, relationships of different variables and sophisticated multivariate analyses on a huge number of variables we have observed. These and more results will be presented during the meeting.

STATISTICAL DATA ANALYSIS

At present the analytical data has been stored in IBM microcomputer programs (Mainly Reflex, Lotus, Dbase III plus and SAS-PC). So far the data has been processed to see any existing gross trends and the data are now being subjected to rigorous statistical tests and analyses, that is, testing for normality (by univariate statistics), homoscadaticity (by t-tests) and independence of observations (by scatter plots). Appropriate transformations (e.g. log, square root, logistic transfer etc.) are being applied to data to satisfy these assumptions for subsequent detailed data analyses. Differences in tree-health parameters (healthy versus declining) and chemical components are being analysed by both a conventional one-way analysis of variance, in conjunction with t-tests (used as a means separation test), and a student t-test (Snedecor and Cochrane 1982). Correlating response variables are being detected by correlation matrices. If response variables do not correlate, analyses of variance with individual chemical concentrations will be done, otherwise correlating variables will be grouped to do multivariate analyses of variance (MANOVA) in a factorial design. General linear models (GLM) will be used for unequal cells. Various regression models (e.g. linear, curvilinear etc.) will be tested to look for trends of changes in sap chemistry in predictor variables i.e. sites and the healthy versus declining trees. Significant differences among chemicals or sites will be examined by Duncan's multiple range test. IBM 4381 Mainframe computer will be used for complex statistical procedures (for example GLM) using SAS under VM/CMS operating system. Basic and Fortran compilers will be used to further modify or reprogram the SAS procedures.

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VOLUME I
SESSION A
AIR QUALITY RESEARCH
POSTER PRESENTATIONS

AP1

Manuscript not submitted.

ESTABLISHING VEGETATION ON EROSION-PRONE LANDFILL SLOPES IN ONTARIO

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While the MOE knew erosion of landfill covers existed, they were unaware of the degree and extent of the problem. The erosion was resulting in: increased infiltration and therefore increased leachate production, reduced aesthetics, nuisance wildlife problems and siltation of adjacent waterways.

This year marks the end of a 3 year study, commissioned to assess the landfill erosion problem and to identify the best available technology to address it. The results of the study will be communicated in a "how to" revegetation manual. A summary of the results of all stages of the project will be presented.

Both the results of the questionnaire and field investigations of 24 representative sites indicated that erosion on Ontario landfills was at least a moderate problem. Almost two-thirds of landfills have apparently never been subject to revegetation efforts after closure. Every open site displayed erosion problems and fully 83% of closed sites were subject to some degree of erosion.

The Landfill Revegetation Manual will have widespread distribution in the province. Graphics and text help explain typical problems such as soil compaction and nutrient deficiency. Keys and flowcharts make finding particular solutions simple.

AP2

SOURCE IDENTIFICATION AND APPORTIONMENT FOR AIRBORNE PARTICLES IN HAMILTON, ONTARIO

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Abstract

Target transformation factor analysis has been applied to elemental compositional data obtained for fine and coarse airborne particle samples taken in Hamilton using a dichotomous sampler. This approach permits the identification of the number and nature of the particle sources as well as providing a quantitative apportionment of the aerosol mass to the identified sources. For the fine fraction particles, the emission sources include motor vehicles, and steel mills. A regional sulfate component was found to contribute significantly to the fine particle mass. For the coarse particles, the sources included road dust, soil, and fugative emissions from the steel mill. The methodology used and the results obtained will be presented.

INTRODUCTION

Ambient air quality standards for total suspended particles (TSP) created the need to identify particle sources so that effective control strategies could be designed and implemented. The initial efforts that are generally made at the identification of particle sources focused on dispersion models of point sources and in most cases, resulted in substantial reductions in TSP levels. However, as the increment of additional control needed to reach standard levels became smaller, the model uncertainties lead to difficulties in identifying the actual sources of continuing problems. In addition, fugitive and other non-ducted emissions are generally not treated or are poorly handled in these models. Thus, additional methods were required to identify and quantitatively apportion particle mass to sources.

Again, the measured properties of the collected ambient samples are used to infer the contributions of the sources to the ambient pollutant concentration. These methods therefore require that samples be obtained at locations of interest, receptor sites, and that the samples so collected be analyzed for the properties that are characteristic of the pollutant sources.

These requirements have arisen at a time when new analytical methods have been developed that permit multielemental analysis of large numbers of airborne particle samples. Thus, large data bases on the composition of airborne particles are available for use in these receptor models. Although much of the thrust of the model developments have been aimed at identification of sources of particle mass, they also can be used to elucidate the origins of the various measured species observed in the samples. It then becomes possible to quantitatively apportion the observed airborne concentrations such as airborne lead among the various source types.

The importance of receptor models as air quality management tools in the United States has recently substantially increased because of the promulgation of a new ambient air quality standard for particulate matter. This new standard requires all of the state and local air quality planning agencies to revise their plans for improving air quality and reducing the particulate level concentrations where they are expected to exceed the prescribed levels. In the associated guidance documents provided by the U.S. Environmental Protection Agency (1986), receptor models are explicitly approved for use in this planning process along with the traditional dispersion models. Thus, receptor models have now become an accepted tool for air quality management.

PRINCIPLE OF MASS CONSERVATION

All of the currently used receptor models are based on the concept of conservation of mass and the use of a mass balance analysis. For example, let us assume that the total airborne particulate lead concentration (ng/m^3) measured at a site can be considered to be the sum of contributions from independent source types such as motor vehicles, incinerators, smelters, etc.

$$Pb_T = Pb_{auto} + Pb_{inc} + Pb_{smelter} + \ldots \qquad (5)$$

However, a motor vehicle burning leaded gasoline emits particles containing materials other than lead. Therefore, the atmospheric concentration of lead from automobiles in ng/m^3, Pb_{auto} can be considered to be the product of two cofactors; the gravimetric concentration (ng/mg) of lead in automotive particulate emissions, $a_{Pb,auto}$ and the mass concentration (mg/m^3) of automotive particles in the atmosphere, f_{auto}

$$Pb_{auto} = a_{Pb,auto} f_{auto} \qquad (6)$$

The normal approach to obtaining a data set for receptor modeling is to determine a large number of chemical constituents such as elemental concentrations in a number of samples. The mass balance equation can thus be extended to account for all m elements in the n samples as contributions from p independent sources

$$x_{ij} = \sum_{k=1}^{p} a_{ik} f_{kj} \qquad \begin{array}{l} i=1,m \\ j=1,n \end{array} \qquad (7)$$

where x_{ij} is the ith elemental concentration measured in the jth sample, a_{ik} is the gravimetric concentration of the ith element in material from the kth source, and f_{kj} is the airborne mass concentration of material from the kth source contributing to the jth sample. There are several different approaches to receptor model analysis that have been successfully applied including chemical mass balance (CMB), and multivariate receptor models including principal components analysis and target transformation factor analysis (TTFA). These models can be applied to both particulate and gaseous species. The basis for each of these methods will be presented in subsequent sections with examples of their application to the identification of particle sources in Hamilton.

CHEMICAL MASS BALANCE

The chemical mass balance (CMB) sometimes called the chemical element balance solves equation 7 directly for each sample by assuming that the number of sources and their compositions at the receptor site are known. The composition of an ambient sample is then used in a multiple linear regression against source compositions to derive the mass contribution of each source to that particular sample.

It must be made clear, however, that the CMB analysis works well in case when both the source and ambient samples were collected and analyzed during the same time period. Much less detailed resolution of sources are generally possible when its sources are not sampled and analyzed. In an intercomparison study organized by the U.S. Environmental Protection Agency (Stevens and Pace, 1984) to examine receptor models, a set of ambient particulate elemental compositional data sets were analyzed by a number of investigators using similar CMB methods. The compositions of particles from sources in Houston were not available and were not measured during this program so that source composition profiles had to be obtained from literature sources. The lack of source data immediately raised problems in the use of the mass balance methods and comparison of results from different investigators (Dzubay *et al.*, 1984). It is not always certain exactly which sources should be included in the analysis. Although emission inventories may be available for the region, it may be that the measured source composition for a coal-fired power plant in Maryland burning eastern bituminous coal is not a particularly good representation for a plant in Hamilton.

An additional problem for receptor modeling is that profiles of real sources change their characteristics in time. For example, the motor vehicle profile is undergoing rapid changes in lead and bromine concentrations with time as the mix of new, catalyst-equipped and diesel cars and leaded-fuel burning vehicles change. Thus, in the absence of adequate source profiles for Hamilton, alternate approaches must be employed.

MULTIVARIATE RECEPTOR MODELS

Alternative methods have been developed for identifying and quantitatively apportioning sources of airborne particles using multivariate statistical analysis. Eigenvector analysis has been the principal method that has been applied to airborne particle composition data. An eigenvector analysis tries to simplify the description of a system by determining the minimum number of new variables necessary to reproduce the measured attributes of the system. The mathematical basis of these methods has been described by Hopke (1985).

Principal components and factor analysis are names given to several of the variety of forms of eigenvector analysis. It was originally developed and used in psychology to provide mathematical models of psychological theories of human ability and behavior (Harman, 1976). However, eigenvector analysis has found wide application throughout the physical and life sciences. Unfortunately, a great deal of confusion exists in the literature in regard to the terminology of eigenvector analysis. Various changes in the way the method is applied has resulted in it being called factor analysis, principal components analysis, principal components factor analysis, empirical orthogonal function analysis, Karhunen-Loeve transform, etc., depending on the way the data are scaled before analysis or how the resulting vectors are treated after the eigenvector analysis is completed. All of the methods have the same basic objective; the compression of data into fewer dimensions and the identification of the structure of interrelationships that exist between the variables measured or the cases studied.

The first step in the eigenvector analysis is the calculation of a dispersion matrix, the matrix that contains quantitative information on the relative variation of pairs of variables or pairs of samples (cases). There are two basic types of dispersion matrices. They are covariance matrices and correlation matrices. For a correlation matrix, the data are scaled such that each variable or each case has an equal weight. The data are not scaled before calculating covariance. In both instances, the data may be centered by subtracting a mean value before scaling and the calculation of the matrix elements. The choice of dispersion matrix depends on the nature of the data set to be analyzed. For many types of chemical spectroscopic data, the covariance matrix is the choice because each variable has the same measurement scale. For many geochemical and environmental problems, the difference in scale between major, minor, and trace components requires scaling to avoid domination of the analysis by the major components.

The dispersion matrix is then decomposed into a series of orthogonal vectors by the process outlined by Joreskog, Klovan, and Reyment (1976) so that

$$U'DU = \Lambda \tag{8}$$

where U is the matrix of eigenvectors, U' is its transpose, D is the dispersion matrix, and Λ is a diagonal matrix of eigenvalues where the trace of Λ is equal to the trace of D. If there were no errors in the data from which D is calculated, the number of non-zero eigenvalues would be the dimensionality of the problem called the rank of D. The rank for the original data matrix is the same as that for the dispersion matrix. However, experimental error generally results in a number of small but non-zero eigenvalues. The determination of the number of vectors containing significant information relative to those dominated by noise is often a difficult one. The lack of universally applicable criteria for determining the dimensionality of the data is a major problem in the application of factor analysis.

In the most commonly used approach to calculating the eigenvectors, the maximum amount of variance is packed into the first eigenvalue. The maximum possible amount of the remaining variance goes into the second and so forth. This compression of the information into a few components permits much of the variation in the data set to be displayed in a two or three dimensional plot. For many classification problems, the first few factors are able to reproduce most of the data structure and to remove some of the noise. The objects can then be plotted using the components axes and thus display the features of high dimensional data in a few dimensions (Blackith and Reyment, 1971). The compression of variance into the first factors will improve the ease with which the number of factors can be determined. However, their nature has now been mixed by the calculational method. Thus, once the number of factors has been determined, it is often useful to rotate the axes in order to provide a more interpretable structure.

The axis rotation can retain the orthogonality of the eigenvectors or cause them to be oblique. Depending on the initial data treatment, the axes rotations may be in the scaled and/or centered space or in the original variable scale space. The latter approach has proved quite useful in a number of chemical applications described by Malinowski and Howery (1980) and in environmental systems as described by Hopke (1985). This method has generally been called target transformation factor analysis.

TARGET TRANSFORMATION FACTOR ANALYSIS

Hopke and coworkers have developed target transformation factor analysis (TTFA). This approach was recently reviewed by Hopke (1988). In this analysis, resolution similar to that obtained from a CMB analysis can be obtained. However, a CMB analysis can be made on a single sample if the source data is known while TTFA requires a series of samples with varying impacts by the same sources, but does not require a priori knowledge of the source characteristics.

In matrix notation equation 3 can be rewritten as

$$X = AF$$

where X is the matrix of ambient aerosol compositions, A is the matrix of source composition profiles, and F is the matrix of mass contributions of the sources to the samples. The objectives of TTFA are 1) to determine p, the number of independent sources that contribute to the system, 2) to identify the components of matrix A, the elemental source profiles, and 3) to calculate F, the contribution of each source to each sample.

The number of sources is determined by performing an eigenvalue analysis on the matrix of correlations between the samples. A target transformation determines the degree of overlap between an input source profile and one of the calculated factor axes. The input source profiles, called test vectors, are developed from existing knowledge of the emission profiles of various sources or by an iterative technique from simple test vectors (Roscoe and Hopke, 1981).

The identified source profiles are then used in a simple weighted least-squares determination of the mass contributions of the sources (Hopke *et al.*, 1980; Severin *et al.*, 1983).

The methodology is described by Hopke (1985; 1988; 1989) and has been successfully applied to a number of urban aerosol mass apportionment problems, artificial data to test the method, and the determination of mineral matter content in coal where the TTFA results could be compared to those obtained by x-ray diffraction. The results presented below were obtained using the TTFA code FANTASIA (Hopke *et al.*, 1983; Hopke and Dharmavaram, 1986).

SOURCE APPORTIONMENT IN HAMILTON

To examine how to apply TTFA to the source apportionment of airborne particulate matter, a data set obtained by the x-ray fluorescence (XRF) analysis of samples collected with a dichotomous sampler in Hamilton during the period of September 19, 1983 to July 7, 1986 will be examined. The dichotomous sampler provides two samples for each 24 hour sampling interval; one sample in the aerodynamic diameter range of 2.5 μm to 10 μm and the other with aerodynamic diameter < 2.5 μm. The larger size range sample is called the "coarse" fraction and the smaller size mode is referred to as the "fine" fraction.

The TTFA process requires data sets that have complete data for all elements in all samples. Thus, samples in which a majority of the data points were below detection limits or those variables for which a majority of the results were undetectable were eliminated. In addition the iterative TTFA procedure also requires knowledge of the total mass concentration value of each sample. For these samples, there had been difficulties in the weighing procedures (Chan, 1988). It is possible that in many cases the radioactive source used as a static eliminator to remove the charge on the filters was not employed or had decayed to the point where it would no longer produce an adequate bipolar charging field. Thus, many of the mass values of the filters are suspect. We have attempted to select as large and complete a data set as possible.

A second difficulty with these data is the absence of quantitative estimates of uncertainty in the measured elemental concentrations. The samples were analyzed by XRF. As part of that analysis, it is possible to estimate the statistical precision in the fluoresced x-ray intensities. By combining these results with the values from the blank filters and estimated uncertainties in the volume of air that was sampled, a quantitative estimate of the uncertainty in the concentration could be obtained. It is strongly recommended to the Ministry that they develop the procedures to incorporate error analysis into the XRF analytical procedures so that the data quality can be fully assessed before further analysis is attempted. It is important to know which values are close to the limits of detection and thus have large inherent uncertainties in them. Furthermore, we have found that the squared average error is typically the most useful weight to use in the iterative target transformation vector development process. Since these errors are not available here, we have used the variances of the variables as the rotation weights. Finally, for those cases where the reported values were below detection limits, we have replaced the detection limit with a value equal to the product of the detection limit with a number between 0 and 1 selected with a uniform random number generator.

Fine Fraction Results

A total of 132 pairs of samples were obtained at site 29025, the site with the longest record of sampling. The other sites in Hamilton had too few samples to permit multivariate analysis methods to be used (Henry *et al.*, 1984). After screening the data for missing values and for designations of questionable analytical results, we have used 94 samples and 21 elemental concentrations for the fine fraction sample data set.

In order to determine the number of resolvable sources, an eigenvalue analysis is made. The results of the eigenvalue analysis are presented in Table I. The eigenvalue provides a measure of the information content of the corresponding eigenvector. The other parameters presented in the table provide measures of the quality of the data reproduced with a given number of factors relative to the original data set. Thus, we want to choose a number of factors such that there is still a significant eigenvalue, but where the values of the data reproduction indicators have become low. In this case, an initial choice of 6 factors is made. There is a significant decrease in the eigenvalue between 6 and 7 factors and there is not a corresponding decrease in the values of the reproduction quality indicators. It is generally not possible to resolve more than about 6 to 7 sources in this type of analysis unless the noise level in the data is very low and there is considerable orthogonality in the source profiles.

The next step is the iterative development of the source profiles. Beginning from the 21 unique vectors and iterating to convergence, a set of 21 final vectors has been obtained. There are a number of the iterated profiles that have quite similar characteristics. In order to group the vectors into a small number of possible source types, a cluster analysis is performed. An agglomerative hierarchical cluster analysis is performed using squared Euclidean distance and

Table I. Results of eigenvalue analysis and data reproduction tests for fine fraction data at Hamilton site 29025.

Factor	Eigenvalue	RMS	Chi-Square*	Exner	Indicator	Average Error
1	8.0864E+01	9.4486E-03	1.8703E-01	.418343	2.0897E-04	978.12
2	7.4554E+00	4.8945E-03	5.3404E-02	.275098	1.5622E-04	763.77
3	2.2110E+00	3.6658E-03	3.1969E-02	.214989	1.3975E-04	717.77
4	1.3004E+00	2.5751E-03	1.6888E-02	.169986	1.2747E-04	669.61
5	9.0204E-01	1.7987E-03	8.8530E-03	.129912	1.1336E-04	539.58
6	7.5265E-01	1.3137E-03	5.0947E-03	.082760	8.4863E-05	484.53
7	2.2998E-01	1.1992E-03	4.6006E-03	.061523	7.4963E-05	314.43
8	9.7348E-02	9.5718E-04	3.1933E-03	.049880	7.3148E-05	310.65
9	7.2979E-02	6.5909E-04	1.6595E-03	.038932	6.9741E-05	307.96
10	5.3833E-02	3.9981E-04	6.7412E-04	.028258	6.2919E-05	302.11
11	1.7576E-02	3.3958E-04	5.4137E-04	.023755	6.7126E-05	309.60
12	1.1989E-02	2.9041E-04	4.4530E-04	.020114	7.3965E-05	284.13
13	1.0466E-02	2.5991E-04	4.0621E-04	.016283	8.0378E-05	213.25
14	6.7278E-03	2.1031E-04	3.0778E-04	.013248	9.1310E-05	153.60
15	4.5323E-03	1.8903E-04	2.9374E-04	.010729	1.0872E-04	98.74
16	3.9014E-03	1.2522E-04	1.5668E-04	.007946	1.2701E-04	73.53
17	2.1127E-03	9.0470E-05	1.0355E-04	.005915	1.6517E-04	40.15
18	1.4441E-03	6.5687E-05	7.3743E-05	.003968	2.2746E-04	23.64
19	7.2716E-04	3.9589E-05	4.0715E-05	.002461	3.8877E-04	9.13
20	2.8266E-04	2.3306E-05	2.8603E-05	.001514	1.3526E-03	3.75

*Chi-square not weighted by errors

average linkage as the clustering criterion (Massart and Kaufman, 1983). The dendrogram for this cluster analysis is provided in Figure 1. The figure shows the relationships among the various vectors. From these patterns, vectors are chosen 6 at a time to reproduce the original data set. The objective is to find a set of vectors that adequately reproduce the original data set. The solution should not produce significant numbers of negative f values since the mass contribution of the sources can only be positive. The program provides the opportunity to test a large number of combinations of source profiles to determine the optimum result. In this case, the combination of Vectors 4, 5, 8, 16, 18, and 21 is very quickly found to provide the best results. Using this combination of vectors, the corresponding F matrix is calculated.

These values are then used in a multiple linear regression analysis along with the mass concentration values to obtain the scaling factors (Hopke *et al.*, 1980; Severin *et al.*, 1983). This analysis provides an additional test of the quality of the analysis. The regression coefficients

```
ITEM NAME        ID NO  A B C D E F G H I J K L M N O P Q R S T U V W X Y

vector 7            7  -I
vector 15          15  -I
vector 2            2  -I-I
vector 6            6  -I I
vector 19          19  -I I
vector 20          20  -I I
vector 3            3  -I-I-I
vector 12          12  -I I I
vector 11          11  -I-I I-I
vector 13          13  -I   I I-------I
vector 4            4  -----I I       I----------------I
vector 17          17  -------I       I                 I
vector 9            9  -------I-------I                I-----I
vector 10          10  -------I                         I     I
vector 5            5  ----------------I--------------I      I---------I
vector 14          14  ----------------I                   I          I
vector 1            1  --------------------I----------------I          I
vector 16          16  --------------------I                            I
vector 18          18  ------------------------------------I-----I   I
vector 21          21  ------------------------------------I      I---I
vector 8            8  ------------------------------------------I
                       A B C D E F G H I J K L M N O P Q R S T U V W X Y
```

Figure 1. Dendrogram of the iterated vectors from the TTFA analysis of the Hamilton fine particle data set.

should be statistically significant, non-negative, and the rescaled profiles should not sum to greater than 100%. If there are negative values, either the wrong combination of vectors was chosen or too many factors were retained. If the rescaled vector sums to greater than 100%, then too few vectors have been used. The analysis can then be redone until an appropriate solution has been obtained. The scaling coefficients for the combination give above is presented in Table II.

From these results, the rescaled vectors can be examined to determine what sources they represent. These vectors are given in Table III. The vectors can be considered in terms of possible sources of airborne particulate matter. Vector 4 has values of Pb and Br as well as Ca. The Br/Pb ratio is 0.30 which is quite typical of aged automotive aerosol (Dzubay *et al.*, 1979). The reaction of the bromine with acidic components of the air such as NH_4HSO_4, H_2SO_4, and HNO_3 leads to the volatilization of bromine as HBr. The lead concentration is 13.2%. This concentration is also quite typical of values observed in the United States before the mandated

Table II. Results of the regression analysis to obtain the scaling factors for the iterative TTFA profiles, Hamilton fine particle data.

No.	Source	Scaling Factor	Uncertainty	t-Ratio
1	vector 4	.2681E+06	1020.	262.8
2	vector 5	.4700E+06	1046.	449.2
3	vector 8	.1818E+06	487.5	373.0
4	vector 16	.1392E+06	854.0	162.9
5	vector 18	.6333E+06	669.0	946.6
6	vector 21	.1005E+06	1042.	96.49

reductions in lead in gasoline. It appears that there was still substantial use of leaded fuel in Hamilton during this time period.

The second source profile has a high value for chlorine and no other significant value. This source could result from the salting of roads to remove ice and snow. There is also a moderate value for potassium. If there were also non-ferrous metals, this source might be

Table III. Source profiles for fine particle Hamilton data (Values are as weight percent).

Element	Motor Vehicles	Salt?	Steel	Soil/ Flyash	Sulfate	Non-Ferrous
Al	2.10	0.97	1.38	11.20	0.65	0.96
As	0.69	0.16	0.00	0.05	0.08	0.00
Br	3.91	0.32	0.52	0.86	0.03	2.69
Ca	3.83	0.00	2.03	4.54	0.00	3.54
Cl	0.03	13.44	0.68	0.47	0.00	6.92
Cr	0.89	0.30	0.03	0.48	0.05	0.08
Cu	1.07	0.22	0.00	0.41	0.08	0.88
Fe	0.52	0.07	39.13	0.01	0.01	3.43
K	2.00	2.06	4.26	3.20	0.16	0.56
Mn	1.00	0.37	2.02	1.20	0.00	1.43
Ni	0.89	0.39	0.00	0.31	0.06	0.02
Pb	13.21	0.81	4.36	2.16	0.12	16.05
P	1.04	0.48	0.27	0.00	0.28	0.00
Rb	0.10	0.36	0.00	0.07	0.12	0.00
Se	0.87	0.18	0.00	0.38	0.03	0.00
Si	2.79	0.18	0.06	44.34	0.02	10.81
Sr	0.35	0.28	0.00	0.14	0.04	0.30
S	0.04	0.03	0.23	0.26	13.89	1.42
Ti	1.01	0.24	0.05	0.64	0.06	0.07
V	0.92	0.29	0.00	0.39	0.05	0.10
Zn	0.05	0.14	0.00	0.73	0.06	50.24

identified as an incinerator. However, both zinc and lead are quite low. Another possible source of chlorine and potassium are wood combustion. It should be remembered that factor analysis identifies elements that covary in time. We normally assume that the covariance is because the elements were emitted by the same source type. The covariance could also arise from other external forces such as local meteorological conditions. Thus, without more detailed understanding of the Hamilton airshed, it is not possible to narrow the range of possible sources of the Cl and K.

The next source has a high iron concentration and very likely represents the nearby steel works. There is high Mn as well as some K, Pb, Ca, and Al associated in the profile. It would require more detailed knowledge of the processes used at the steel works to determine the source(s) of these additional elements. High Al and Si concentrations are found in the "Soil" source profile. The Al/Si ratio appears correct for soil or flyash, but the absolute concentrations are high. However, attempts at a 7 factor solution failed to obtain a satisfactory solution. The low Fe value in this profile is probably due to the presence of the Steel source. Since it is almost a unique factor for Fe, it variation dominates the covariance of iron with the other elements and masks the presence of Fe in the Soil source profile. It is also possible that the "Soil" profile also represents some impact from coal flyash. The volatile elements such as As and Se that are generally enriched in the surface layer of flyash particles are one of the species upon which soil and flyash can be distinguished. Although As is reported above detection limits, the proximity of its K_α emission line (10.532 keV) to the strong L_α line (10.54 keV). Thus, As is generally not well determined by XRF. In this profile, Se does appear to be enriched. Thus, there is likely to be some contribution of coal flyash to the soil particles in these samples.

The next source is regional sulfate. This source type is universally observed in the fine particle source apportionment. It represents emission sources of SO_2 upwind of Hamilton sufficiently far that the SO_2 has been transformed into $SO_4^=$. The value of 13.2% S in the Sulfate source is somewhat lower than has been observed in other locations where values around 20% S have been observed (Dzubay *et al.*, 1988; Alpert and Hopke, 1981). However, it is similar to values observed at industrialized locations in the St. Louis area (Liu *et al.*, 1982; Severin *et al.*, 1983; Chang *et al.*, 1988). Such a value suggests the presence of carbonaceous secondary aerosol components. Since carbon is not measured by XRF, it cannot be accounted for directly in the analysis. If it covaries with one or more of the measured elements, the mass contribution from carbon is properly accounted for in the analysis. If there were a carbon source that does not contain measured elements, then the analysis can encounter considerable difficulties in accounting for all of the measured particle mass (Hopke *et al.*, 1989).

The final profile has high concentrations of Cl, Fe, Pb, Si, and Zn with Pb and Zn represent 66% of the total profile mass. This profile could be from a non-ferrous metal operation. Since the nature of the steel-making processes and the chemical factories in the vicinity of the sampling site are not well known, it is not possible to be more specific in relating this source profile to particular industrial activities.

The mass contributions to the various elemental concentrations that are observed in these samples are presented in Table IV. For example, Pb is approximately equally distributed between the motor vehicles, steel, and non-ferrous sources. It also provides an indication of the quality of fit for each element. It will be observed that the average fit of the elements to the average concentrations are quite good. However, some elements have a large dispersion in the quality of the fit. Aluminum has an average point-by-point uncertainty of 19.4% whereas arsenic has a value of over 1600%. Thus, there is much poorer ability to predict an individual

Table IV. Mass contributions of the various sources to the observed elemental concentrations.

Element	Motor Vehicles	Salt?	Steel	Flyash/ Soil	Sulfate	Non-Ferrous	Avg Pred Contrib.	Avg Obs Contrib.	Avg % Error
Al	.176E-01	.267E-01	.410E-01	.138E+00	.122E+00	.679E-02	.352E+00	.349E+00	19.4
As	.575E-02	.442E-02	.000E+00	.621E-03	.145E-01	.000E+00	.253E-01	.191E-01	1608.6
Br	.326E-0i	.887E-02	.154E-01	.106E-01	.471E-02	.191E-01	.913E-01	.871E-01	83.4
Ca	.320E-01	.129E-04	.604E-01	.561E-01	.136E-06	.251E-01	.174E+00	.162E+00	41.8
Cl	.263E-03	.371E+00	.201E-01	.581E-02	.121E-04	.490E-01	.446E+00	.447E+00	138.2
Cr	.742E-02	.813E-02	.768E-03	.590E-02	.885E-02	.540E-03	.316E-01	.320E-01	527.0
Cu	.896E-02	.602E-02	.000E+00	.501E-02	.158E-01	.625E-02	.420E-01	.403E-01	254.8
Fe	.433E-02	.184E-02	.116E+01	.672E-04	.172E-02	.243E-01	.120E+01	.120E+01	1.3
K	.167E-01	.567E-01	.127E+00	.395E-01	.290E-01	.395E-02	.273E+00	.261E+00	33.3
Mn	.835E-02	.101E-01	.602E-01	.148E-01	.839E-04	.102E-01	.104E+00	.105E+00	88.6
Ni	.739E-02	.107E-01	.000E+00	.379E-02	.120E-01	.110E-03	.340E-01	.289E-01	1387.8
Pb	.110E+00	.224E-01	.130E+00	.267E-01	.227E-01	.114E+00	.425E+00	.430E+00	5.4
P	.871E-02	.132E-01	.797E-02	.000E+00	.526E-01	.000E+00	.824E-01	.853E-01	106.8
Rb	.828E-03	.983E-02	.000E+00	.904E-03	.231E-01	.000E+00	.346E-01	.187E-01	2068.6
Se	.729E-02	.489E-02	.000E+00	.470E-02	.585E-02	.000E+00	.227E-01	.210E-01	2901.8
Si	.233E-01	.490E-02	.190E-02	.547E+00	.457E-02	.766E-01	.658E+00	.661E+00	4.4
Sr	.292E-02	.781E-02	.000E+00	.176E-02	.800E-02	.210E-02	.226E-01	.144E-01	1818.5
S	.338E-03	.833E-03	.671E-02	.326E-02	.260E+01	.101E-01	.262E+01	.262E+01	.1
Ti	.840E-02	.675E-02	.136E-02	.785E-02	.109E-01	.502E-03	.357E-01	.362E-01	303.1
V	.766E-02	.796E-02	.000E+00	.478E-02	.923E-02	.695E-03	.303E-01	.271E-01	957.7
Zn	.381E-03	.378E-02	.684E-04	.896E-02	.107E-01	.356E+00	.380E+00	.379E+00	5.3

value of arsenic than an individual value of aluminum. In general the elements with large uncertainties are those low in concentration and therefore have many values near the detection limits. The results presented here are fairly typical of those observed in the kind of analysis.

Finally the contribution of the source types to the airborne particle mass contributions can be determined. The mass contributions in $\mu g/m^3$ can be examined as a function, of sampling date. But there are no strongly discernable patterns in these results. However, the intermittent nature of the sampling schedule, particularly in the latter part of the time period, makes it difficult to have a sufficient continuous time record to discern temporal patterns in the results. Thus, the TTFA has provided an indication of the types of sources contributing particles to the observed airborne concentrations and the amount of mass contributed by those sources and represent the type of results that can be expected of such an analysis. At this time, the results for the coarse particle samples are still being analyzed. We have not yet found a suitable solution. Once an acceptable solution has been obtained for the coarse samples, we will be able to examine the overall pattern of source contributions to the observed airborne particulate concentrations in downtown Hamilton.

Acknowledgement

This report was prepared for the Ontario Ministry of the Environment as part of a Ministry funded project (No. 311PL). The views and ideas expressed in this report are those of the author and do not necessarily reflect the views and policies of the Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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AP3

A Year Experience with the Air Quality Index System for Ontario

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1. Introduction

In order to better inform the public on the quality of Ontario's air, a new Air Quality Index (AQI) was implemented in May-June of 1988. The AQI system offers a comprehensive coverage consisting of 33 monitoring sites in 26 cities across the province. The index cities are Metropolitan Toronto (consisting of Toronto, East York, North York, York, Etobicoke and Scarborough), Hamilton, Windsor, Sarnia, Sudbury, St. Catharines, Niagara Falls, London, Kitchener, Waterloo, Guelph, Burlington, Oakville, Oshawa, Mississauga, Sault Ste Marie, Thunder Bay, North Bay, Cornwall, Ottawa and Kingston. The system provides hourly information for six basic pollutants (sulphur dioxide (SO_2), suspended particles (SP), nitrogen dioxide (NO_2), ozone (O_3), carbon monoxide (CO), and total reduced sulphur compounds (TRS)) and informs the public on a real-time basis. The previous Air Pollution Index (API), a combination of SO_2 and SP, still serves as a regulatory tool and in addition, is incorporated as a sub-index of the AQI system.

2. The Air Quality Index

The Ontario AQI (Shenfeld, 1987; Shenfeld and Yap, 1989) is similar in design to that of the Canadian Index of the Quality of Air (Young et al., 1977) and that of the U.S. EPA Pollutant Standards Index (Ott and Hunt, 1976). The descriptive categories and numerical values, however, are related to Canadian standards (Federal and Ontario) which differ from that of the United States for each of the pollutants. A sub-index ranging from zero upwards is related to the hourly concentration of each of the pollutants. As the index increases, the air quality decreases. The sub-index is calculated for each pollutant based on its effect and the highest sub-index at any time becomes the AQI.

The Index values are divided into five descriptive categories and reflects possible effects on health, vegetation, property, and aesthetic values.

0 - 15	very good
16 - 31	good
32 - 49	moderate
50 - 99	poor
≥ 100	very poor

3. The Telemetry System

A new air quality telemetry system has been acquired and implemented to handle the vast amount of data collected. This system logs, transmits, and processes air quality and meteorological data from 120 monitoring stations across the province. Each instrument is interrogated every two seconds and five-minute averages are stored at local loggers and are thus available to local air pollution control agency personnel. The data is then automatically transmitted from each of six regional processing units to the Ontario Air Quality Computer Center in Toronto. Here, hourly and other cumulative hourly averages, the AQI, the API, and as well, hourly, daily, and monthly reports are generated. The performance of the system is reflected in the success rate of obtaining good quality data. Over the past year, the validity of data was over 95% for most locations. An example of the percentage of time that valid O_3 readings were obtained to produce the AQI is shown in Fig.1.

4. Publicizing the Index

The AQI levels for each City are currently sent to the new media eight times daily at the following hours:

Midnight, 4:00 A.M., 6:00 A.M., 7:00 A.M., 11:00 A.M., 2:00 P.M., 4:00 P.M. and 8:00 P.M. except when the Index at a location is 32 or above. When this occurs, the Index is issued hourly until the air quality improves to the Good range (i.e. < 32). Air quality forecasts are also issued four times daily (7:00 A.M., 11:00 A.M., 2:00 P.M. and 4:00 P.M.). An example of an air quality forecast is given below:

AIR QUALITY INDEX FORECAST FOR: THURSDAY, SEPTEMBER 21, 1989

Generally good to very good. Possibility of moderate levels due to SP at some sites of southern Ontario this morning and a slight possibility of moderate levels due to TRS at Cornwall.

There is much interest in the Index from the media and the public when the air quality is in the Moderate and Poor ranges.

5. AQI Data Analysis

Data for the 12 month-period June 1988 to May 1989 were analysed. In general, Good to Very Good air quality levels (AQI < 32) prevailed at all sites throughout the province for most of the year (96% of the time or better). Elevated air quality levels occurred at all sites, except Thunder Bay in northwestern Ontario. Fig.2 shows the frequency that AQI levels were in the Moderate and Poor ranges at each of 21 cities (only downtown locations in Metro Toronto, Hamilton and Windsor). There were no incidences of Very Poor air quality reported at any location. As can be seen from Fig.3, ozone is by far the most frequent cause of high index readings in Ontario (74%). This was followed by suspended particles (16%) and total reduced sulphur compounds (8%).

The ozone excursions, confined to the warm season, were often widespread and associated with long-range transport of air pollutants into and across southern Ontario. There appears to be also some contribution of local sources to the elevated ozone levels, especially across or near highly urbanized areas of the province. On a number of occasions, moderate AQI values were associated with nocturnal O_3 exceedances, especially in northeastern Ontario. The incidences of SP excursions occurred throughout the year with some bias towards the morning hours of peak traffic, low-level temperature inversions, and light winds. For TRS, excursions were more localized to areas associated with pulp and paper, petroleum refineries, and iron and steel industries. On a few occasions, moderate AQI levels were associated with SO_2 in Sudbury and with the API in Hamilton. Carbon monoxide and nitrogen dioxide did not result in a high index reading during the study period.

Concluding Remarks

The new Air Quality Index system in Ontario has been successfully implemented and has been in operation for over a year now. It has been used to better inform the public on the quality of Ontario's air on a real-time basis, 24 hours per day, seven days per week.

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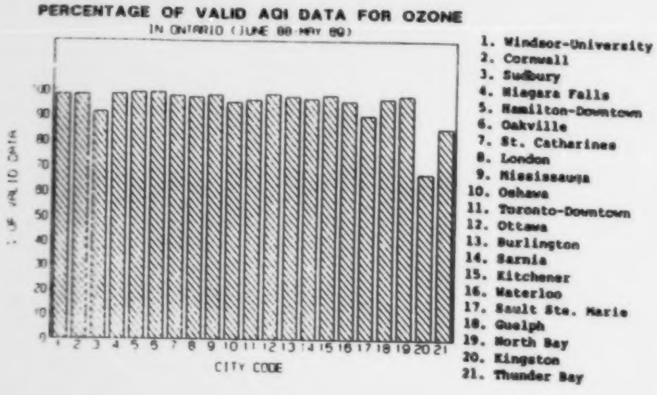

Fig. 1

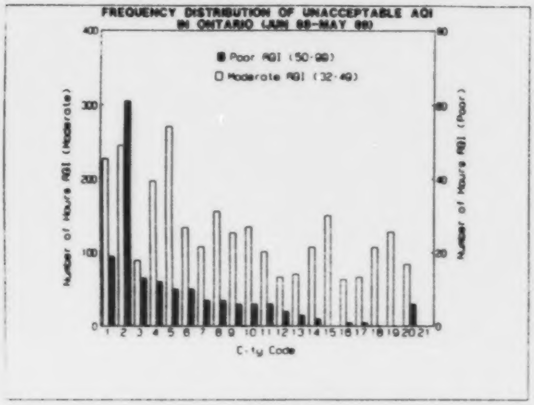

Fig. 2

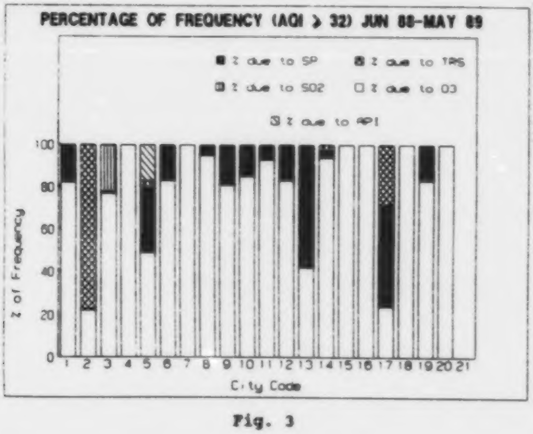

Fig. 3

1. Windsor-University
2. Cornwall
3. Sudbury
4. Niagara Falls
5. Hamilton-Downtown
6. Oakville
7. St. Catharines
8. London
9. Mississauga
10. Oshawa
11. Toronto-Downtown
12. Ottawa
13. Burlington
14. Sarnia
15. Kitchener
16. Waterloo
17. Sault Ste. Marie
18. Guelph
19. North Bay
20. Kingston
21. Thunder Bay

AP4

RISK ASSESSMENT WITH COMPLEX MIXTURES

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In recent years increasing public attention has focussed on the risk associated with a wide range of air borne pollutants. Risk assessment in such cases faces two major problems i.e. (a) the duration and cost of whole animal studies and (b) the extrapolation of data obtained with individual chemicals to more natural systems involving several chemicals often of varying proportions. The first problem has been addressed by the use of 'short term' tests i.e. tests of reasonable cost which extend over at most days or weeks rather than years. Although more than a hundred such tests have been developed involving a wide range of organisms most published work has involved a relatively small number of tests. In our work we have used both the Ames and micronucleus assays.

The second problem i.e. the effect of chemicals in mixtures has proven much less amenable to solution.

Researchers have known for many years that chemicals when combined often elicit mutation rates different from either their individual or combined (added) mutation rates. In such cases (i.e. non-additive) the effects were usually said to be synergistic (greater than additive) or inhibitory (less than additive). However neither the type nor the extent of non- additivity has been predictable. As a result many authors have described their results only qualitatively. Attempts to explain non-additivity have usually involved considerations such as depletion of a nutrient or competition for S9. The underlying assumption of such an approach is that chemical interactions in a short term assay are a form of 'multi body' problem in which a solution can at best be approximated but not made exact.

Our approach suggests that the effect of chemical combinations can be predicted by an approach related to that involved in multi-enzyme systems.

Materials and Methods

Chemicals: we have used nine chemicals, five PAHs and four chlorinated hydrocarbons. i.e. Benzo(a)pyrene (BaP) 7,12 dimethybenz(a)anthracene (DMBA), 1-nitropyrene (INP) dibenz(a,h)anthracene (DBA), benzo(b)fluoranthene (BF), 1,1,1,-trichloroethane, 1,1,2,2, tetrachloroethane, carbon tetrachloride and methylene chloride. All were purchased from Aldrich Chemical Company. B6C3F1 male mice (Harlan Sprague Dawley Inc) of age 7-8 weeks have been used for *in vivo* bone marrow micronucleus assay.

Short Term Assays

Standard protocols for the mouse bone marrow micronucleus assay and Ames assay have been used. In the latter case tester strains TA98 (frame shift mutation) and TA100 (base substitution mutation) have been used with and without S9 activation.

Results and Discussion

(a) Individual Chemicals

Each chemical has been tested extensively in each assay and standard dose response curves have been plotted. In most cases the closest approximation to linearity is achieved when the $\log_{10}$ dose is plotted against response. For most chemicals the response falls off at higher doses due to toxicity. In such cases (which substantially exceed 'natural' exposures) subsequent testing involved only doses from the initial ascending dose response area. The activities of each chemical are listed below:

Chemical	Mutagenicity				
	Ames Assay				Micronucleus Assay
	TA98		TA100		
	(-S9)	(+S9)	(-S9)	(+S9)	
BaP	-	+	-	+	+
DMBA	-	+	-	+	+
INP	+	+	+	+	-
DBA	-	+	-	+	+
BF	-	-	-	+	+
1,1,1 trichloroethane	-	-	-	-	+
1,1,2,2 tetrachloroethane	-	-	-	-	-
Carbon tetrachloride	-	-	-	-	-
Methylene chloride	+	+	+	+	-

(b) Pairwise chemical combinations

Pairwise chemical combinations have been tested in both assays with equivalent doses of each chemical (by weight). Of the 36 possible pairwise combinations, those involving at least one mutagenic chemical all produce mutagenicity responses which differ from strictly additive and these differences include examples of both synergism and inhibition.

(c) BaP and DMBA

The variety of responses noted above suggested that we look initially at one pair of chemicals in more detail. BaP and DMBA are promutagens and it has been known for some years that when administered together they produce a less than additive response [Salamone *et al* (Can. J. Genet. Cytol. 21 101, 1979) predicted that this effect is due to interaction with the S9 fraction]. Our approach has been to vary the relative proportions of the two chemicals and measure the resulting mutagenicity at each combined dose in the Ames assay.

Under these conditions the surviving activity (actual dose response slope/additive response) can be measured for each concentration. When the resulting activity is plotted against chemical proportions a linear relationship of the form Activity = K $\log_{10}$ [BaP]/[DMBA] can be demonstrated. From this function and knowing the concentrations of each we can predict with good accuracy the mutagenicity of any proportions of the two. (The relationship starts to fail when proportions differ by more than about 80:1). K values for any pair of chemicals can be determined and we are now clarifying the relationship for mixtures of three where Activity A,B,C = $F[K_1(AB), K_2(BC), K_3(AC)]$.

Acknowledgement

The generous support of The Ontario Ministry of the Environment is gratefully acknowledged.

AP5

GENETIC TOXICOLOGY OF LUNG CELLS IN VIVO

by

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ABSTRACT

By means of a new assay that we have devised it is possible to measure both chromosomal aberrations and gene mutations induced in vivo in the lung. The new assay makes it feasible to test chemicals according to the Canadian Guidelines for Mutagenicity Testing (Health & Welfare, Canada, and Environment Canada) and should be particulary suitable for respired chemicals.

Two types of genetic damage are involved in oncogene activation, point mutations and chromosome aberrations. These two types of genetic events are induced in different proportions by the various agents which cause genetic damage and are detected by different means. An assay which measured both types of events in cells which have experienced the same genetic damage would improve the chances of detecting the significant events. Due to complex physiological, metabolic and pharmacokinetic parameters that cannot be reproduced *in vitro*, *in vivo* assays are more relevant to human toxicology. Here we report an *in vivo* assay in which both types of genetic damage can be reliably detected and quantified. The assay uses lung fibroblasts.

Previous work by Dean and Senner (1977) indicated that gene mutations could be measured by cloning techniques in lung cells of Chinese hamsters. They used 8-azaguanine as a selective agent and reported that they could detect diethylnitrosoamine which is difficult or impossible to detect in the bone marrow micronucleus assay (Heddle et al 1983). We have adapted and improved the procedures in several ways. First, we used 6-thioguanine -- which is more stable in culture -- as a selective agent and confirmed that we could routinely and reliably detect mutations induced *in vivo* in lung cells. Second, we improved the plating efficiencies of the cells dramatically by changes in the tissue culture methods. Third, we added the ability to detect increased frequencies of chromosomal aberrations in the same cells after *in vivo* exposure to four model mutagens. This was done by scoring the frequency of micronuclei after adding cytochalasin B to the cultures according to the method of Fenech and Morley (1985). This technique avoids the possibility of grossly underestimating the clastogenicity of a treatment due to toxicity of the test agent.

To establish the reliability of the assay at measuring gene mutations and chromosomal aberrations concurrently, four model mutagenic carcinogens were tested. The four model mutagens we used were chosen in order to encompass agents producing very different spectra of the genetic damage that can be induced by various agents. The results reflect this: X-rays and ethyl nitrosourea produced both chromosomal aberrations and gene mutations. In contrast, ethyl methane sulphonate produced large numbers of mutations but no chromosomal aberrations. Methyl methane sulphonate produced the inverse pattern of ethyl methane sulphonate, namely chromosomal aberrations but no mutations. Given the specificity with which oncogenes are activated by one or the other type of damage, not all carcinogens would be picked up by an assay which relied on either endpoint alone. This is not to say that some of these four fail to cause both types of damage: it may be that the 'missing' effect would have been seen using larger sample sizes or at more extreme doses. It may seem a disadvantage of in vivo studies that extreme doses cannot be used resulting in reduced sensitivity. This may, on the other hand, be an advantage as it may prevent false positives which could result from non-physiological treatment conditions such as hypertonicity (Brusick,1987).

Dean and Hodson-Walker (1979) presented evidence suggesting that tissues which were targeted by an agent in terms of tumour production, also showed an increase in the mutation frequency. One might expect that this correlation would not hold in all cases due to the fact that oncogene activation specifically requires one or the other type of genetic event. While tissue specificity may be an advantage for basic research and detecting pulmonary carcinogens, it may result in false negatives when screening agents active at other sites. Because the lungs are immediately 'downstream' from the liver they will be the first tissue to be exposed to the metabolites generated in the liver, after the liver itself. Hence they should be one of the most exposed tissues in which to detect the mutagenic effects of carcinogens.

We have tested urethane (ethyl carbamate), a model lung carcinogen of great potency, by dissolving it in water and administering it i.p. An increase in the number of mutations was detected -- greater than 7 times the historical spontaneous frequency -- but there was no increase in chromosomal aberrations. Urethane is, however, a potent clastogen in the bone marrow.

We next tested four chemicals by inhalation. They were ethylene oxide, methylene chloride, perchloroethylene, and peroxyacyl nitrate (PAN). The animals were exposed in glass inhalation chambers which were designed and built at York. No increase in either the mutation frequency or the number of chromosome aberrations was detected using any of these agents in the first set of experiments which are now in the process of being repeated.

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ACKNOWLEDGEMENTS

This work was supported by grants from the Ontario Ministry of the Environment and from the Strategic Grants Program of the Natural Science and Engineering Research Council, to whom we are grateful.

AP6 CONFIGURATIONS FOR EFFICIENT COLLECTION OF FLUORESCENCE RADIATION FROM CHEMICALLY-SELECTIVE LIPID MONOLAYERS AND MULTILAYERS

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The development of fibre-optic chemical sensors (FOCS) may currently be divided into three phases. 1. The development of device structures for maximizing efficiency and miniaturization while reducing cost. The miniaturization criterion has resulted in most experiments using fluorescence as the operating signal, owing to its high sensitivity and the well developed associated theory. 2. Investigation of different selective chemical or biochemical systems which are candidates for optical detection schemes. 3. Studies of the immobilization of selective systems such that the resulting optical signal may be maximized while sufficient selectivity and activity is maintained. This report is concerned with these three phases of sensor development.

MOLECULAR RECEPTORS AND THE GENERIC LIPID MEMBRANE

The primary thesis of this work is that protein which can bind selectively to a specific organic or biochemical species, can be incorporated into an ordered fluorescent lipid membrane assembly such that selective binding events lead to changes in the lipid structure (transduction) which can be measured quantitatively by fluorescence intensity variations. The primary advantage of this method of detection is that it is applicable to interactions of enzymes, antibodies, receptors and lectins, and therefore provides a sensitive generic strategy for sensor application.

Recent work by our group involved the use of molecular receptor (Acetylcholine receptor, AChR) interaction with a target ligand (carbamyl choline, Carb) as a model system(1). What was demonstrated using bilayer lipid membrane vesicles was that the AChR could be labelled with the fluorescent probe nitrobenzoxadiazole (NBD), and that an enhancement in fluorescence intensity occurred when the labelled AChR reacted with Carb. Reproducibility of that experiment was improved by obtaining enhancement values for the protein-bound fluorophore at one wavelength and for an unaffected component at a second wavelength. The ratio of enhancements at both wavelengths compensated for variations of parameters such as instrumental drift and activity of the receptor.

Similar enhancement was observed when the label was attached only to 1% of the lipid molecules present, leaving the receptor unlabelled. This illustrated the potential of lipid systems to act as generic transducers of selective complexation events, allowing for the characterization of a single system for subsequent use with different selective agents.

Another molecule which selectively binds with AChR is the snake venom a-bungarotoxin (a-btx). It was observed that the initial complexation with a-btx caused an increase in fluorescence similar to that observed with the Carb, with sensitivity at the nanomolar concentration level. While being able to detect both analytes was seen as useful, a problem was the inability to distinguish which was being detected.

The use of fluorescence as a signal introduces the multidimensional aspects of fluorescence into the analysis. The characteristics of intensity, wavelength, lifetime and polarization may be determined concurrently. This enables comparison of signals, which in some cases may be used to compensate for instrumental variations and correct for interferences, but also may be used to better characterize the selective interaction occurring(2).

LIFETIME ANALYSIS DISTINGUISHES ANALYTES

Time decay curves for NBD-PE labelled vesicles containing AChR were obtained at various wavelengths, with most analysis being done at the peak wavelength of 550 nm. Adequate fits were obtained only with two exponential components, indicating the model to be applied was:

$$I(t) = A1 \exp(-t/T1) + A2 \exp(-t/T2)$$

where I(t) is intensity at time t, A's are the coefficients and T's are the exponential decay times or "lifetimes" of the components. For these experiments, T1 was ~1 ns while T2 was ~5 ns. Attaching physical significance to these parameters is somewhat arbitrary, though models such as the longer lifetime being derived from membrane components in regions closer to the large, relatively immobile proteins are reasonable.

Time-resolved fluorescence intensity enhancement was observed after addition of Carb to a concentration of 100 uM and after addition of a-btx to a concentration of 1 uM. This was seen as a change in the total value of the coefficients (A1 + A2) of the exponential components, and may be compared to a simple intensity increase as in previous experiments (1). What was different in this case was that the change in the relative contributions of the two components was different for the enhancement due to the Carb from that due to the a-btx. This may be measured by taking the relative contributions and examining the ratio of each. The ratio, R = A2/A1, was reasonably constant at 550 nm between trials. The change in R was 0.45±0.07 for Carb addition and 0.25±0.26 for a-btx addition, indicating that the lifetime could indeed be used for distinguishing between the two types of binding agents.

MONOLAYER CHARACTERIZATION AND DEPOSITION

Characterization of stearic acid monolayers at the air water interface consisted of examination of the compression isotherms, and also involved measurements made with a fluorescence microscope positioned over a Langmuir film balance. This enabled the collection of fluorescence intensity data at the air/water interface, which corresponded to measurements made of vesicles using the spectrofluorimeter. As well, fluorescence images showing the phase structure in the monolayer were concurrently collected. The image intensity showed that the relative fluorescence quantum yield of the NBD-PE molecules decreased as the compression proceeded; this is opposite to what would be expected based on a simple mobility/collisional quenching model. In the images collected at surface pressures approximating the pressure in lipid bilayers, the NBD-PE molecules are actually partitioning into less ordered domains in the monolayer. This partitioning indicates the growth of condensed phase domains in the fluid phase monolayer, where the fluorophore is then excluded from the more dense phase in a system composed of two phases in co-existence.

Fluorescence images obtained from monolayers of stearic acid that were deposited onto quartz wafers by Langmuir-Blodgett casting processes, indicated retention of the phase structure established at the air-water interface. Intensity measurements were done by integration of the fluorescence spectrum. There was an intensity increase as small volumes of acetic acid solution were added to the solution in which the wafer was immersed. This was consistent with results previously observed with vesicle systems. Responsiveness of the stabilized monolayer was confirmed, indicating that membranes fabricated in this manner may be capable of transducing other perturbations.

One potential use of this initial system may be as a means of detecting pH changes. An enzyme, acetylcholinesterase, was added to the subphase of the film balance under the microscope. After allowing the enzyme to partition to the surface under a stearic acid monolayer (12 hrs.), the substrate acetylcholine was injected as a 2 uM solution into the subphase. The result was an increase in the overall intensity which then decayed over a few minutes. This was exactly what would have been expected in the case where the enzyme hydrolysed the substrate, producing choline and acetic acid. No change was observed in the image, (though massive rearrangement would be slow), but the monolayer did become noticeably brighter for a time. This would indicate that rearrangement of the NBD-PE in the monolayer would have to occur at a sub-microscopic level to yield the observed effect.

A NEW DETECTION CONFIGURATION USING A PYROELECTRIC SENSOR

Our previous reports to the Ministry of the Environment have considered light-guiding and evanescent wave detection schemes for collection of a fluorescence signal. An exciting alternative transduction method would couple the advantages of fluorescence methods and optical fibres with an extremely sensitive low power pyroelectric detector (portable).

Electronic relaxation to the ground state can occur via several pathways. In addition to photon emission, one of the pathways is through radiationless de-excitation, which produces local heating (3). This local heating results in temperature fluctuations in the sample material and the production of a thermal wave. Materials which are pyroelectric generate an electric current as a result of a temperature differential across the thickness of the substance. This can be detected by use of metal films (electrodes) that are deposited on both surfaces of the pyroelectric material to monitor voltage fluctuations across the material. The change in temperature induces a polarization of the pyroelectric material, producing a dipole moment in the direction of the temperature gradient. The result is a current flow and a net voltage across the pyroelectric(4,5). In general, temperature changes on the order of 10-6 K can be detected(3).

Several materials are available for use as pyroelectric detectors. Plastic films like polyvinylidene fluoride (PVDF) are a recent development in pyroelectric detection. Although having poorer sensitivity (p = 3 x 10-9 C cm-2 K-1) that some other ceramic systems, they can be produced in different shapes and are very inexpensive (5,6). The operating temperature range of PVDF is from -40 °C to 100 °C, making it highly versatile.

Pyroelectric detectors function optimally as thin films. This property makes them ideal for spectroscopic absorption measurements of samples having low optical density, high optical density, light scattering and specular reflection (7). Monolayer surface phenomena can be studied using pyroelectric detectors.

By specifically using gold as the electrode metal on the PVDF film, deposition of sulfur terminated molecules (such as lipids and selective proteins) on to the electrode can be done using the self-assembly properties of sulfur-gold bonding. This type of stabilizing surface, which participates in a selective reaction, combined with the high pyroelectric sensitivity of PVDF, can be used as the basis for chemical sensor design. Our experimental results for fluorophores such as fluorescein isothiocyanate and eosin isothiocyanate on PVDF show that chemical sensors can be based on a pyroelectric transduction mechanism having submonolayer sensitivity and spectral selectivity.

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AP7

ATMOSPHERIC DEPOSITION OF CHLORINATED COMPOUNDS IN THE GREAT LAKES BASIN.

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Introduction

Atmospheric deposition is an important pathway by which chlorinated organic compounds enter the Great Lakes. Total polychlorinated biphenyls (PCB) and organochlorine pesticides have been reported in rain and snow samples collected in the Great Lakes basin since the mid-1970s (*e.g.* Murphy and Rzeszutko (1977) and Strachan and Huneault, (1979)). These compounds are ubiquitous and are often detected even in isolated locations. Long range transport has been implicated for the movement and wide distribution of chlorinated organic compounds throughout the Great Lakes basin (Swackhamer *et al.*, 1988).

Chlorinated organic compounds are monitored by the Deposition Monitoring Group of the Air Resources Branch at four rural, shoreline sites around the Great Lakes (Pt. Petre, Port Stanley, Shallow Lake and Turkey Lake) , an urban shoreline site near Toronto and inland at Dorset (Figure 1). Dorset is a rural site, with no known local sources of the target compounds. The Dorset site provides a basis upon which background levels and sampling precision may be estimated and serves as a long-range transport receptor site. The Toronto Island site is part of the Remedial Action Plan (RAP) for the Toronto waterfront and is representative of an urban environment. The major objectives of the organic deposition monitoring network are to determine the identity and concentrations of trace organics in air and precipitation and to quantify atmospheric deposition of toxic trace organics to the Great Lakes.

A summary of mid-1988 to mid-1989 concentration data of some chlorinated organic compounds in air and precipitation is presented here. The data reported is more precise than earlier data (*e.g.* Orr *et al.* 1988) because of increased analytical sensitivity. Greater sensitivity was achieved in part by increasing analyte concentrations in the sample extracts.

Methods

Precipitation inputs of organochlorine pesticides and PCB are collected over 28 days with automated M.I.C. Type B wet only collectors. A gravity-fed XAD-2 resin adsorbent column concentrates non-polar semi-volatile organic compounds *in situ*. A glass-fibre particulate filter is located upstream (Figure 2). Sample volumes are usually greater than 10 litres over 28 days. Sampler efficiency is typically 80-90%. High volume (Hi-vol) air samplers incorporating glass-fibre filters and XAD-2 resin cartridges are used to sample for chlorinated pesticides and PCBs in air (Figure 3). Airflow is controlled at 0.42 m^3/s. Volumes collected are approximately 2500 m^3. over 4 days. Analysis for total PCB and organochlorine pesticides is based on solvent extraction and evaporation of the extract to increase the analyte concentration factor, florisil column fractionation and dual column high resolution gas chromatography with electron capture detection (HRGC/ECD). The compounds are identified by their retention times and quantitated by measurement of peak areas relative to calibration standards.

Results and Discussion

Summary statistics for precipitation are reported for HCB (Hexachlorobenzene), total PCB (sum of individual congeners) and α- and γ-BHC (Hexachlorocyclohexane) for the period April 1988 to April 1989 (Table 1). Summary statistics for air are reported from September 1988 to April 1989 (Table 1). All data are reported as concentrations for filter plus cartridge. PCB, HCB, and α- and γ-BHC are the most commonly detected compounds in precipitation and air. Other species (*e.g.* DDT group and chlordane) are observed only intermittently and are not reported here. PCB are found in 68% of all precipitation samples analyzed. HCB, α-BHC and γ-BHC are found in 37%, 39% and 22% of precipitation samples. Reported positives (samples with target compound concentrations greater than minimal detection limits) are much greater in air samples. Percentage of air samples with reported positives ranges from 79.5% for PCB to 75% for γ-BHC. Air data are considerably greater than minimum levels of detection because of the large sample volumes collected.

Very few positives were reported for precipitation samples collected during 1986 and 1987 (Orr *et al.*, 1988). Using a limited number of samples, volume weighted concentrations were reported by Reid *et al.* (1988) for 1987 data. HCB ranged from 0.03-0.39 ng/l, α-BHC from 0.37-8.30 ng/l and γ-BHC from 0-2.4 ng/l. Volume weighted mean concentrations for 1988/89 data are comparable to these results (Table 1). The 1988/89 data were obtained using a more sensitive analytical method. Sensitivity was enhanced overall by increasing the analyte concentration factor. Sensitivity for PCB was improved through quantitation of specific congeners. This decreased detection limits by 2 orders of magnitude for PCB but only by a factor of 2 for HCB, α-BHC and γ-BHC. The relatively low percentage of positives reported in this paper for all of the target compounds except PCB imply that precipitation concentrations for many of the target compounds remain at or below the detection limit.

Within site variability in precipitation concentrations of the target species is generally greater than that between sites (Table 1). It is not known why PCB concentrations in precipitation are much greater at Dorset and Pt. Petre. It is interesting that elevated PCB levels are also reflected in the air samples from these sites. There are no local PCB sources near Dorset or Pt. Petre. HCB, α- and γ-BHC and PCB concentrations in air are relatively uniform both within and between sites. Air concentrations are comparable to data reported at other continental locations in North America and Europe (e.g. Bidleman *et al.*, 1988 and Atlas and Giam, 1988) and to those reported by Orr *et al.* (1988) for 1987 air samples collected at Dorset and Port Stanley.

Conclusions

Preliminary data have been presented from a network operated by the Ontario Ministry of the Environment. There is good general agreement between these results and other findings in the literature. The following areas to improve the monitoring effort have been identified and should be addressed:

Recommendations

1) The data presented here are preliminary and limited to relatively few sites. No data is available from the western end of Lake Superior or from Lake Michigan. The network needs to be expanded to include more sampling sites to improve representativeness and properly characterize Great Lakes deposition. At least 2 sites should also be collocated as a quality control.

2) Data are available for only a single year. Data must be collected over a period of several years to characterize long term atmospheric inputs and identify processes and seasonal variability in deposition.

3) Sampling methods need to be extended to distinguish between organic inputs in rain, snow, particle deposition and vapour exchange. In particular methods need to be developed to quantify dry deposition. Dry deposition is very difficult to quantify because of the inadequate size of the data set and large uncertainty in estimating deposition velocities.

4) Analytical sensitivity is inadequate to quantify many chlorinated organic species in precipitation. Methods to improve sensitivity (i.e alternative analytical methods or by increasing sample volume) need to be investigated.

4) Because of the expense in operating a sampling network for chlorinated organics or other compounds it is essential that there be close coordination between different monitoring groups to avoid duplication of effort and to enhance information exchange.

5) A quality assurance program needs to be incorporated into the monitoring effort to ensure that the data quality characteristics of accuracy, precision, completeness, representativeness and comparability are attained.

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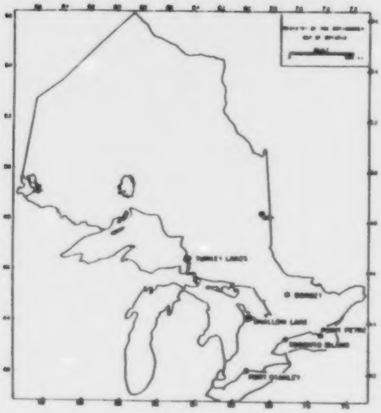
TURKEY LAKES
DORSET
SHALLOW LAKE
POINT PETRE
TORONTO ISLAND
PORT STANLEY

FIGURE 1 MONITORING SITE LOCATION MAP

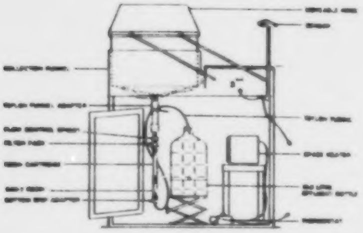

FIGURE 2 MIC B PRECIPITATION SAMPLER

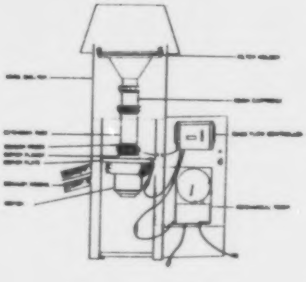

FIGURE 3 HIVOL AIR SAMPLER

TABLE 1: SUMMARY STATISTICS OF SELECTED CHLORINATED ORGANIC COMPOUNDS IN PRECIPITION AND AIR. LIMITS OF DETECTION (LOD) IN PRECIPITATION (10 LITRES) ARE 0.05 NG/L FOR HCB, α-BHC AND γ-BHC AND 0.02 NG/L FOR PCB. LOD IN AIR (2000 M³) ARE 0.001 NG/M³ FOR HCB, α-BHC AND γ-BHC AND 0.0004 NG/L FOR PCB.

	PRECIPITATION (NG/L)				AIR (NG/M³)			
SPECIES	HCB	PCB	α-BHC	γ-BHC	HCB	PCB	α-BHC	γ-BHC
PORT STANLEY		N=12[1]				N=16		
ARITH. MEAN	0.10	10.78	0.91	0.52	0.05	0.28	0.21	0.03
MINIMUM	0.00	00.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.90	43.10	4.00	4.00	0.19	0.77	1.14	0.17
1QUARTILE	0.00	00.00	0.00	0.00	0.01	0.05	0.06	0.01
3QUARTILE	0.04	14.85	1.85	0.25	0.07	0.41	0.25	0.04
VWMEAN[2]	0.09	11.62	0.97	0.24				
DORSET		N=11				N=14		
ARITH. MEAN	0.11	74.86	0.38	0.14	0.07	0.41	0.04	0.01
MINIMUM	0.00	2.30	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.40	298.40	2.20	1.00	0.34	3.43	0.16	0.05
1QUARTILE	0.00	22.00	0.00	0.00	0.02	0.07	0.00	0.00
3QUARTILE	0.20	113.50	0.40	0.20	0.07	0.34	0.08	0.02
VWMEAN	0.13	81.79	0.36	0.12				
SHALLOW LAKE		N=12				N=10		
ARITH. MEAN	0.06	7.52	2.30	0.61	0.03	0.19	0.10	0.01
MINIMUM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.40	46.00	17.80	4.70	0.08	0.46	0.33	0.04
1QUARTILE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3QUARTILE	0.05	8.10	1.10	0.65	0.06	0.40	0.17	0.03
VWMEAN	0.07	8.12	0.96	0.26				
TURKEY LAKE		N=12				N=16		
ARITH. MEAN	0.12	21.70	1.65	0.33	0.05	0.18	0.13	0.02
MINIMUM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.80	105.00	8.30	3.10	0.12	0.66	0.31	0.03
1QUARTILE	0.00	0.00	0.00	0.00	0.01	0.02	0.05	0.01
3QUARTILE	0.16	18.25	2.50	0.00	0.07	0.37	0.20	0.02
VWMEAN	0.11	21.49	1.18	0.27				
PT PETRE		N=12				N=11		
ARITH. MEAN	0.72	78.49	0.10	0.00	0.07	0.39	0.17	0.02
MIMIMUM	0.00	13.81	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	3.30	179.20	0.60	0.00	0.15	1.01	0.52	0.07
1QUARTILE	0.20	35.90	0.00	0.00	0.04	0.03	0.07	0.00
3QUARTILE	0.42	100.70	0.00	0.00	0.11	0.64	0.22	0.03
VWMEAN	0.37	57.43	0.23	0.00				
TORONTO ISLAND		N=12				N=16		
ARITH. MEAN	0.02	25.26	0.92	0.26	0.07	0.40	0.10	0.02
MINIMUM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAXIMUM	0.20	111.20	7.40	2.70	0.30	2.33	0.32	0.08
1QUARTILE	0.00	0.00	0.00	0.00	0.02	0.11	0.03	0.00
3QUARTILE	0.00	43.90	0.30	0.00	0.10	0.41	0.13	0.03
VWMEAN	0.04	16.08	0.63	0.17				

[1] N EQUALS THE NUMBER OF SAMPLES

[2] VOLUME WEIGHTED MEAN

AP8

IGNITION STUDIES OF SELECTED EXPLOSIVE MIXTURES OF GASES AND DUSTS EMITTED FROM CEMENT KILNS

I.I. Inculet, G.S.P. Castle, E.J. Weckman, K.A. Shelstad and M.L. Wick

The operation of cement plants generates considerable quantities of dust which generally are collected by means of electrostatic precipitators. Inside the cement kilns, the calcination process is accompanied by the formation of carbon monoxide, hydrocarbons and other combustible gases which, under certain conditions, may form explosive mixtures. The cement industry monitors the kiln emissions of carbon monoxide and oxygen continuously. If an impending or already formed explosive mixture is detected, the electrostatic precipitators are immediately de-energized. The decision to shut down the precipitators currently is premised on very safe limits for allowable concentrations of combustible gas, without taking into account the unknown influence of substantial concentrations of cement dusts present in the kiln exhaust gases. This study includes analyses of actual exhaust gas samples from cement kilns and results from flammability tests conducted on representative clean gas mixtures and various gas/cement dust mixtures.

Cement Kiln Exhaust Gas Composition

Kiln exhaust gas and dust loading samples were collected from both inlets and outlets of the electrostatic precipitators at two cement plants, each running different process streams. Two sets of 12 samples each were collected at various times at the inlets and outlets of the precipitators and each sample was analyzed for gas composition using a gas chromatograph. Dust loading was measured using thimble filters in which the dust was collected for a specified time period. A summary of the average results is in Table 1. In all cases, the variations in gas concentrations were within 7% of the mean. In no test was an upset condition encountered in the process stream, so these results provide a good indication of background gas concentrations and dust loadings under normal operating conditions. The results compared well with reference values estimated by plant personnel.

Results in Table 1 indicate that typical concentrations of CO_2 and N_2 are 25% and 63% respectively in the inlet and outlet gases of the precipitators at both plants. Concentrations of CO varied considerably from 0.1% in Plant A to 0.03% in Plant B. Concentrations of H_2 and unburned hydrocarbons (UBHC), composed mainly of methane, exhibited some variability with time, but were present only in very small concentrations for normal operating conditions. In Plant 2, the O_2 concentration was typically 6%, but in Plant 1 it changed from 4-7.5% between samples A and B. This was due to substantial modifications in the process stream so sample B is thought most representative of normal operating conditions. A comparison with published explosion limits for single gases indicated that a mixture containing any one of the flammable gases at these concentrations would not ignite in the electrostatic precipitator (1).

Representative dust loadings, as shown in Table 1, lie in the range from 30-550 g/m^3. The literature suggests that for volatile dusts, dust/air mixtures with loadings of 100 g/m^3 could ignite under certain conditions, while loadings of 10-80% inert dust could suppress explosion even for very high ignition energies (2). Thus, it was decided to test the full range of dust loadings measured in the cement plant kiln exhaust and to extend the range depending on the initial results.

Flammability Testing of Kiln Exhaust Gases

The Apparatus

A versatile experimental explosion chamber was built to test the flammability of representative clean gas and gas/dust mixtures. The apparatus is shown schematically in Figure 1 with more details of the chamber in Figure 2. The system is a modified version of the 20-litre test chamber used by the U.S. Bureau of Mines (3). It has been shown to produce repeatable

Table 1: Average gas concentrations and dust loadings measured in Cement Plants 1 and 2

Plant	Sample No.	Position	CO_2	O_2	N_2	CO	H_2	UBHC	Dust Loading
			Volume %						g/m^3
Plant 1	A	Inlet	28.5	3.6	64.7	0.13	< 0.02	< 0.06	32.7
	A	Outlet	26.0	4.8	63.6	0.098	N/D	< 0.03	6.7
	B	Inlet	21.4	7.4	N/D	0.15	N/D	N/D	N/D
	B	Outlet	not taken						
Plant 2	A	Inlet	24.0	6.1	61.0	0.011	N/D	N/D	514.1
	A	Outlet	23.1	6.5	63.3	0.014	N/D	N/D	< 15.0
	B	Inlet	24.9	6.1	63.41	0.034	N/D	N/D	573.2
	B	Outlet	24.6	6.4	63.9	0.021	N/D	N/D	< 2.0

measurements of minimum ignition energy for gases, dusts and gas/dust mixtures (2,3). The volume of the present chamber is 25.5-litre. It is equipped with a pressure transducer and fine shielded thermocouple for detection of the explosion. For each test, the chamber is purged with N_2, evacuated and filled with the inert gases by partial pressure and the flammable gases using displacement columns. Mixing is accomplished through the fill procedure and enhanced using a fan inside the chamber. Final gas compositions were cross-checked using a batch gas sample, analysed on the gas chromatograph. No major discrepancies were noted. Ignition was accomplished with a custom electric spark apparatus. It consisted of a high voltage power supply and variable capacitor unit. This allowed easy determination of the spark energy as there were fewer losses than would be incurred with a coil ignition system.

Results and Discussion

Characterisation of the Apparatus

Operation of the explosion chamber was tested by running a series of explosions on H_2/air mixtures with N_2 as the diluent. It was found that explosions occurred for H_2 concentrations of greater than 6% and less than 32% with O_2 concentrations of 7% and 6% respectively. These values correspond well to those found in the literature indicating that the explosion vessel was operating correctly (1).

Flammability of Gas Mixtures Without Dust

In the initial stage of this testing, mixtures of gases typical of those found in the cement kilns (listed in Table 1) were put in the explosion chamber and tested. None of these mixtures ignited, even with spark energies of up to 40J. This was expected since, under normal operating conditions, the probability of explosion in the cement plant is very low. The danger in operation occurs when the process undergoes an upset in conditions since transients could increase the concentrations of flammable gases to levels that would lie within explosive limits for the mixture. In this study, it was assumed that such transients might increase the concentrations of flammable gases by as much as 50 times. This would increase the concentrations of CO to 7.5%, of H_2 to 1% and of CH_4 to 3%. It was not known whether this mixture would explode, since the flammability limits for many multiple gas mixtures have not been recorded previously.

To test the limits of flammability of gas mixtures similar to those postulated for upset conditions, a base mixture composed of 25% CO_2, 8% O_2 and 1.5% CH_4 was chosen. The proportions of CO, H_2 and N_2 in the mixture were varied individually and in combination to find the lean flammability limits. For a mixture as above but also containing 2.5% CO, the amount of H_2 was increased from 0.1% to greater than 30% (with corresponding decreases in the quantity of N_2). In no case did the gas mixture explode. This result is not consistent with expectations and currently is being investigated further. A second mixture as above, but with 1% H_2 was used to test varying proportions of CO and N_2. It was found that explosions occurred for mixtures containing greater than 10% CO. When the percentage of H_2 was increased to 3%, explosions occurred in mixtures with only 7.5% CO. The results are shown with other published data in Figure 3 (4). The agreement is good and clearly indicates the sensitivity of flammability limits to concentrations of all flammable gases, particularly when they are found combined in a mixture.

Flammability of Gas Mixtures With Dust

An independent set of tests was conducted to investigate the flammability limits of gas/dust mixtures similar to those found in the kiln exhaust. The base gas was chosen as 25% CO_2, 8% O_2, 1.5% CH_4, 7.5% CO, 3% H_2 and 55% N_2. To this were added various amounts of cement dust that had been collected at the plants. It was found that very small concentrations of dust, less than 4 g/m^3, did not prevent explosion of the gas mixture. Concentrations just higher than this, greater than 6 g/m^3, prevented explosion of the mixture for the period while there was dust between the electrodes, but the gas mixture did explode after the dust was allowed to settle to the floor of the chamber. Therefore, the limiting concentration of dust, in suspension, which will make a flammable gas mixture inert lies between 4 and 6 g/m^3. From these preliminary tests, it is evident that cement dust in suspension will render an explosive mixture inert; however, it remains to be seen if there are effects of background gas composition or dust composition on the dust concentrations required to prevent explosions.

Conclusions

1. Samples of kiln exhaust gas and cement dust indicate that, under normal operating conditions, the concentrations of flammable gas are well below those required to form an explosive mixture, while the concentrations of cement dust are higher than those required to make an explosive gas mixture inert.

2. Under upset conditions, it is conceivable that explosive gas mixtures might be formed; however, in this preliminary study, it was demonstrated that small quantities of cement dust in suspension would render a mixture of explosive gases inert. It remains to be seen if there are effects of background gas composition or dust composition on the dust concentrations required to prevent explosion in an electrostatic precipitator.

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4. Personal communication, A.K. Deshpande, Ontario Ministry of the Environment.

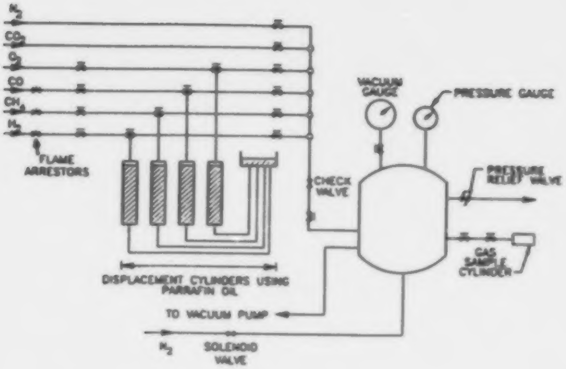
N2
CO2
O2
CO
CH4
H2
FLAME ARRESTORS
DISPLACEMENT CYLINDERS USING PARRAFIN OIL
TO VACUUM PUMP
N2
SOLENOID VALVE
CHECK VALVE
VACUUM GAUGE
PRESSURE GAUGE
PRESSURE RELIEF VALVE
GAS SAMPLE CYLINDER

Figure 1: Schematic diagram of the explosion chamber and associated gas handling system.

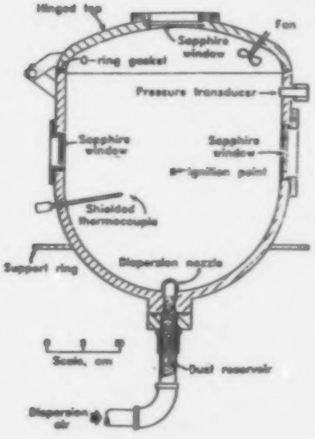
Hinged top
Sapphire window
Fan
O-ring gasket
Pressure transducer
Sapphire window
Sapphire window
Ignition point
Shielded thermocouple
Support ring
Dispersion nozzle
0 5 10
Scale, cm
Dust reservoir
Dispersion air

Figure 2: Details of the explosion chamber with instrumentation (3).

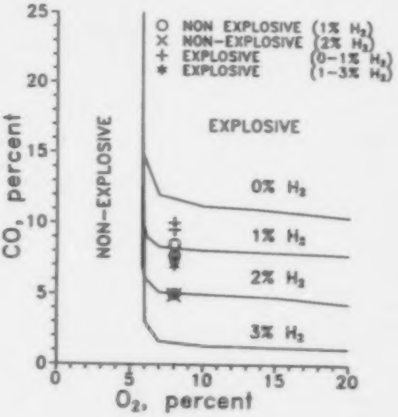

Figure 3: Comparison of present results with previously published flammability data (4).

AP9

ON TWO-PHASE FLOW MODELING OF WIND-INDUCED PARTICLE-EROSION RATES WITHIN A TURBULENT BOUNDARY-LAYER

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Abstract

In order to assess the impact of open area sources on local airsheds, a prediction of the mass flux emitted from the sources is required. It has been shown that the wind-induced uplift of particles is a function of the local surface friction velocity which changes with downwind distance due to the presence of particles. Thus, the interaction between the particle or disperse phase and the wind or carrier phase dictates the amount of material released into the environs. A numerical two-phase flow model using a two-equation turbulence model has been developed to take into account the extra momentum source term generated by the presence of uplifted particles in the boundary-layer. Initially, the saltation and suspension of particles results in a slowing down of the surface wind speed and therefore the quantity of material emitted tends to decrease. Subsequently, the uplifted particles return to the surface causing some other particles to be uplifted and, more significantly, allowing the boundary-layer to speed up and induce more particles to become mobile. Thus, a "moving equilibrium" between the mass transport and the boundary-layer is reached. The carrier-phase transport equations of mass, momentum, and kinetic energy and its dissipation rate are solved in an Eulerian frame of reference. A stochastic Lagrangian approach is used with respect to the dispersed phase. The preliminary results of the model are in agreement with experimental data.

Introduction

The vertical mass-flux from an undisturbed open area is the result of wind-induced saltation of the mobile soil/sand particles on the surface. Investigators have developed empirical relationships for the vertical and horizontal fluxes as a function of the surface shear velocity (u_*) and other parameters. The first empirical relationship for the saltation rate (Q) was proposed by Bagnold (1941) as

$$Q \propto u_*^3 \tag{1}$$

This has been modified and extended (White, 1982) to include various parameters and is the basis of most calculations for determining the erosion rate associated with a surface. The empirical relationships provide estimates of the material transported by the wind but do not lead to any further understanding of the physics of the processes.

An approach for gaining an understanding of the interactions between saltation mass-flux and the wind is to consider the mass-flux in terms of individual particles in a Lagrangian frame of reference. In the present work, such an approach is considered with respect to wind-erosion in a turbulent boundary-layer. In particular, a procedure for linking a stochastic Lagrangian particle-trajectory model with an Eulerian model of the fluid motion is outlined. We note that this procedure serves as the basis for a two-phase flow approach to the modeling of the saltation process.

Lagrangian Particle-Trajectory Model

In the present case, the particles can be considered spherical, and the requisite equation of motion can be derived from a force balance on an individual particle as follows. Newton's second law yields:

$$m_p \frac{d\bar{V}_p}{dt} = \sum \bar{F}_i, \tag{2}$$

where m_p is the particle mass, V_p is the particle velocity and ΣF_i is the sum of the relevant forces comprising drag, lift, pressure, gravity and virtual mass (Ciccone, et al, 1989). The resultant equation after rearrangement is

$$\left[\frac{\rho_p}{\rho_f}+C_{vm}\right]\frac{d\bar{V}_p}{dt} = -\frac{3}{4}C_d\frac{\bar{V}_R|\bar{V}_R|}{D}+\left[1+C_{vm}\right]\frac{d\bar{V}_f}{dt}-\left[\frac{\rho_p}{\rho_f}-1\right]\bar{g}-C_l\,(\bar{V}_R\times\bar{\Omega}), \tag{3}$$

where C_d, C_l and C_{vm} are the coefficients of drag, lift and virtual mass, respectively, g is gravity, D is the particle diameter, ρ_p and ρ_f are the particle and fluid densities, V_R is the particle relative velocity and V_f is the fluid velocity.

Since $\rho_p >> \rho_f$, the above equation can be reduced to the following, with only the drag, lift and gravity forces being retained:

$$\frac{d\bar{V}_p}{dt} = -\frac{3}{4}C_d\frac{\rho_f}{\rho_p}\frac{\bar{V}_R|\bar{V}_R|}{D} - C_l\frac{\rho_f}{\rho_p}(\bar{V}_R\times\bar{\Omega})-\bar{g}. \tag{4}$$

This equation provides a Lagrangian description of the particle path. The drag coefficient C_d, varies with the particle Reynolds number

$$Re_p = \frac{|\bar{V}_R|\,D}{\nu}, \tag{5}$$

and is calculated from empirical relationships (Morsi and Alexander, 1972). The lift force is the result of the vector product of $\bar{V}_R$ and the fluid vorticity ($\bar{\Omega}$). The latter is given by,

$$\bar{\Omega} = \bar{\nabla}\times\bar{U} = (0,0,-\frac{\partial U}{\partial y}), \tag{6}$$

where $\partial U/\partial y$ is the mean gradient of the mean streamwise velocity component (Hunt, et al, 1984). Thus, the circulation around a particle with relative velocity $\bar{V}_R$ is,

$$\bar{V}_R\times\bar{\Omega} = (-V_{Ry}\frac{\partial U}{\partial y},\ V_{Rx}\frac{\partial U}{\partial y},\ 0). \tag{7}$$

The equation of motion (7) can be resolved into x and y components, which are:

$$\frac{dV_{px}}{dt} = -\frac{3}{4}\frac{C_d}{D}\frac{\rho_f}{\rho_p}V_{Rx}|V_R| + C_l\frac{\rho_f}{\rho_p}V_{Ry}\frac{\partial U}{\partial y}, \qquad (8a)$$

and

$$\frac{dV_{py}}{dt} = -\frac{3}{4}\frac{C_d}{D}\frac{\rho_f}{\rho_p}V_{Ry}|V_R| - C_l\frac{\rho_f}{\rho_p}V_{Rx}\frac{\partial U}{\partial y} - g. \qquad (8b)$$

Given an initial particle velocity and position and the wind field, (8) can be integrated numerically, both forward and backward in time, to determine the particle impact and ejection points and velocities. By *randomly* varying the wind field components and ensemble averaging the trajectories, a stochastic description of the particle's trajectory can be realized. It should be noted, that the fluid has been assumed to be unaffected by the presence of the particles.

Two-Phase Flow Considerations

The Lagrangian model described above does not take into account interactions between the fluid and the particles, i.e., the model assumes that the fluid is unaffected by the presence of particles. Studies carried out by Bagnold, White and others have shown that the wind field is altered by the particles. Bagnold (1941) found that a substantial change in the wind velocity profile occurs during saltation. This indicates that a coupling between the fluid or carrier phase and the particle or dispersed phase is required to accurately predict the transport of particles during erosion events.

Two approaches can be utilized in the treatment of two-phase flows, Eulerian and Lagrangian. In the Eulerian approach, the carrier and dispersed phases are both treated as continua and the appropriate governing equations are solved (Durst et al., 1984). In the Lagrangian approach, the carrier phase is still treated as a continuum but the dispersed phase is considered to be made up of a set of discrete particles. The trajectories of the particles are calculated via Newton's second law, and with the particle locations and velocities known, the mass, momentum and energy transfers between phases can be calculated. This amounts to a statistical formulation of the problem, since a finite number of particles must be used to represent a very large number present in the carrier phase.

Equation (8) provides the instantaneous velocity of the dispersed phase which is coupled with the carrier phase through its instantaneous velocity. The mean velocity components of the carrier phase are obtained from the solution of the time-averaged Navior-Stokes equations, in conjunction with a two-equation turbulence model. The fluctuating component of the carrier velocity is randomly chosen from an isotropic Gaussian distribution with mean-square value of 2/3 k, where k is the turbulence kinetic energy of the carrier-phase flow. After an elapsed particle travel-time (t_p) equal to a turbulence characteristic time, a new fluctuating component is chosen. The characteristic time is chosen as the lesser of the dissipation time scale of the turbulent eddies and the residence time of the particle in the eddy, i.e., the dissipation length scale divided by the particle relative velocity (V_R).

For each particle present, the particle's equation of motion is integrated over as many time intervals as required to traverse a specified distance. Once a sufficiently large number of particles is used, the behavior of the dispersed phase will be accurately represented.

The transfer of momentum between phases is caused by to the drag force. It can be shown (Durst et al, 1984) that the momentum source term in the carrier phase due the presence of particles is equivalent to the difference in particle-velocities into and out of a control volume multiplied by the mass flow rate represented by the specific particle. This additional source term is used in solving the carrier-phase momentum equations.

Acknowledgments

This research was supported by the Ontario Ministry of the Environment, Grant 372G.

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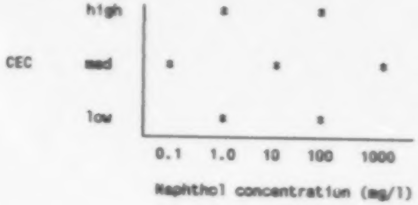
AP10

GROWTH EFFECTS OF NAPHTHALENE AND NAPHTHOL ON PLANTS: THE ROLE OF SOIL TYPE IN MODIFICATION OF TOMATO, RADISH AND SWISS CHARD RESPONSES. B.A. Marie* and D.P. Ormrod, Department of Horticultural Science, University of Guelph, Guelph, ON, N1G 2W1

The phytotoxicity and potential for contamination of vegetables by organic compounds of industrial origin is of increasing concern to members of both public and private sectors. While a considerable data base on the uptake and accumulation of agricultural organic chemicals by vegetation exists, a similar data base for industrial organic compounds is scanty. The information on agricultural chemicals cannot be readily transferred to industrial contaminants, as the molecular characteristics of the two groups of compounds are quite different. The uptake of organic compounds from soil or air by plants is dependent on numerous parameters, including the size and water solubility of the compound, and the tendency of the compound to adhere to soil particles. This latter characteristic is to a large extent dependent of the soil type, in particular the amount of organic material, and the relative tendency of a soil to sequester organic molecules may be indicated by the cation exchange capacity (CEC). Due to the wide range of soil types which may be encountered in a natural or agricultural ecosystem, it is desirable that a dose-response relationship be developed to describe the response of plants to ranges of contaminant concentration and soil types. The objective of this study, therefore, was to determine the dose response relationship between concentration of naphthalene or naphthol at the root, cation exchange capacity of the rooting medium and growth of tomato (*Lycopersicon esculentum* cv. New Yorker), radish (*Raphanus sativus* cv. Cherry Belle) and swiss chard (*Beta vulgaris* cv. White King)). The dose response relationships were determined using an incomplete factorial experimental design known as a partial central composite rotatable, analysis of covariance for the reduction of plant-to-plant variation, and polynomial regression for description of the relationship (Marie and Ormrod, 1986; Ormrod *et al.*, 1984).

Seeds were sown in either Promix BX (high cation exchange capacity), a mixture of sand and Promix BX (low cation exchange capacity) or a mixture of vermiculite and Promix BX (medium cation exchange capacity), at a rate of three seeds per pot. The pots were then placed in a controlled environment chamber which delivered a day/night temperature regime of 25/20°C, each for 12h, canopy level photosynthetically active radiation at 325 $\mu E\ m^{-2}s^{-1}$ for a 16h photoperiod and 70% relative humidity (Ormrod *et al.*, 1980). Planting was staggered in order that germination of all three species occurred on approximately the same day. Three days after germination, seedlings were thinned to one per pot, and the plants were grown for three more weeks. During this period, they were irrigated with half-strength Hoegland's nutrient solution as required, when the soil appeared dry. On day 22, planar leaf area of swiss chard and radish, and plastochron index of tomato, were estimated for use in analysis of covariance. Following covariate measurement, the plants were placed in exposure cubes with environmental conditions similar to those in the controlled environment growth chambers. Two ml of naphthol or naphthalene in ethanol were applied to the soil; plants were harvested on the third day after application of the contaminant. Foliar injury, as well as fresh and dry weights of shoot (divided into stem, leaf and hypocotyl where applicable) and leaf area were assessed on the plants. The experimental design was an partial central composite rotatable, with seven contaminant concentration/soil CEC combinations (Figure 1).

Figure 1: Treatment combinations for partial central composite rotatable experimental design.



The central treatment (CEC=med, naphthol concentration=10 mg/l) is repeated twice for each replication of the other points, in order that all areas of the response surface have approximately equal estimates of variance. The treatment means were summarized by polynomial functions in the second order for both factors, including an interaction term. Preliminary results (first two of four replications) indicated that there was differentiation among the treatment means for each species (Table 1).

Table 1: Treatment means for growth response of tomato, radish and swiss chard grown in rooting media with different CEC's, to various concentrations of naphthol.

CEC	low		med			high	
[nap]	1.0	100	0.1	10	1000	1.0	100
Tomato							
LFW	2.27	2.43	3.16	2.39	1.76	2.67	2.08
LDW	.211	.251	.306	.240	.216	.249	.232
LA	87.8	94.7	118	90.3	60.7	101.3	74.9
Radish							
LFW	3.96	4.12	6.06	5.35	4.63	6.04	5.22
LDW	.416	.409	.554	.452	.533	.432	.466
LA	107	111	174	141	124	161	142
Swiss chard							
SFW	3.21	2.25	4.16	5.29	1.66	4.06	3.61
SDW	.246	.263	.306	.334	.220	.272	.299
SA	64.0	48.2	84.0	102	46.9	83.3	76.9

LFW and LDW are leaf fresh and dry weights, respectively, the units of which are g/plant. SFW and SDW are shoot fresh and dry weights, respectively, the units of which are g/plant. LA and SA are leaf and shoot area, respectively, the units of which are cm^2/plant.

When the data which are summarized in Table 1 were subjected to regression analysis, most growth parameters were related to CEC more strongly than to concentration of naphthol (Table 2). For all growth parameters, a significant portion of the total sum of squares was accounted for by the covariate, indicating that a significant reduction in error sum of squares was realized, leading to improved precision of the experiment (data not shown). This contribution of analysis of covariance to the detection of plant response has been noted for gaseous air pollutant studies (Ormrod *et al.*, 1983). Also not shown are the data for growth response of radish hypocotyl and tomato stem, for which there was little of significance, mainly due to large variation in the data. It should also be noted that naphthalene caused virtually no growth response in these three species, likely due to its low solubility in water; those results are not reported here.

Table 2: Polynomial coefficients which describe the relationships between growth of tomato, radish and swiss chard, and CEC of rooting media and concentration of naphthol.

	CEC	[nap]	CEC x [nap]
Tomato			
LFW	+L, -Q	ns	-
LDW	+L, -Q	ns	ns
LA	+L, -Q	ns	ns
Radish			
LFW	+L, -Q	ns	ns
LDW	+L, -Q	ns	ns
LA	+L, -Q	ns	ns
Swiss chard			
SFW	+L, -Q	ns	ns
SDW	+L, -Q	+L, -Q	ns
SA	+L, -Q	ns	ns

+L indicates linear coefficient with a positive sign; -Q indicates quadratic coefficient with a negative sign; - indicates negative interaction; ns indicates no significant regression coefficients; linear and quadratic coefficients significant at $P \leq 0.10$.

Although Table 1 indicates that both concentration of naphthol and cation exchange capacity of the rooting medium are related to growth response of these species to this compound, it is clear from the regression analysis in Table 2 that CEC is the more important determinant of growth response to naphthol, and that there is little interaction between these two factors in those responses. This suggests that the concentration of compound available to the plant is determined more by soil type than by the applied dose, within the ranges of the two factors utilized in this study. Finalization of the dose response relationships, in the form of quantification of the polynomial coefficients, will further characterize the relative importance of the linear and quadratic components.

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AP11 A METHOD OF INTEGRATION FOR GAS-PHASE AIR CHEMISTRY MODELS

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1. Introduction

Gas-phase chemistry is an important component in regional and global air chemistry or air pollution models. The numerical simulation and analysis of gas-phase chemical reactions in the atmosphere can be difficult, due to the complexity of the reactions taking place (hundreds to thousands in the real atmosphere) and the computation time required to yield an accurate solution. Various techniques have been used in the past to simplify the reactions and/or reduce the number of species while still maintaining a realistic representation of atmospheric processes. Even with reduced reaction sets the computation time remains a problem, particularly when many simulations of atmospheric chemistry are desired. For example, a four minute simulation of the 81 reactions and 46 species of the RADM mechanism (Stockwell, 1986) using a standard algorthm (DIFSUB, Gear, 1971) requires 36 seconds of CPU time on the U of T Cray XMP-24 computer. Long time simulations of 2 to 3 days of chemical reactions can thus become prohibitively expensive, using standard techniques. Alternative methods of analizing reaction sets and/or performing numerical integrations are therefore required.

2. Dunker's Method

A method was proposed by Dunker (1984, 1986) to overcome this computational problem. The technique is based on Taylor series expansions of final chemical concentrations with respect to initial concentrations, over a time interval δt . The first and second order coefficients of the expansion objectively describe the reaction mechanism's sensitivity towards its initial conditions. The coefficients may be used to determine the importance of a given chemical towards later states of the reacting system.

These coefficients may also be used as a form of numerical integration through the evaluation of a Taylor series in the initial values of the model parameters. Numerical integration thus becomes a matter of retrieving a set of coefficients from memory and evaluating a single equation for each chemical in the reaction set - this can be done in 89 lines of standard Fortran code. Using this method, the computation time of a simulation can be decreased by over two orders of magnitude. The method requires a larger amount of development time than the implementation of a standard integration package; this investment is considerably offset by later reductions in processing-time.

3. Use of Dunker's Method at U of T.

Dunker's method has been developed and tested for the RADM reaction mechanism. The aim of the study was twofold: (1) to analyze the RADM reaction set using sensitivity coefficients in order to determine which chemical species were the most important towards acid precipitation, and (2) to evaluate Dunker's numerical integration method in order to determine its accuracy as a means of numerical integration. The work was done as part of an Eulerian Long-Range Transport modelling project.

Five sets of initial concentrations ranging from a very polluted to a very unpolluted atmosphere were used to generate sensitivity coefficients for later analysis. An iterative technique was used to determine which chemicals' initial concentrations had the greatest effect on later values on a subset of species important to cloud chemistry. It was found that the chemicals whose initial values have the greatest influence on acid precipitation are: (NO_2 , NO, O_3 , HONO, peroxyacetylnitrate, H_2O_2 , HCHO, higher aldehydes, SO_2 , toluene, xylene, olefins, gaseous H_2O , CH_4 , ethane, higher alkanes, CO, HNO_3 , HNO_4 , NO_3 and N_2O_5) . The initial concentrations of stable product species had no effect on subsequent chemistry. Similarly, the initial values of organic peroxides and peroxyacetic acid had little effect on later chemistry, since these species usually appear as products in the RADM reaction set. The initial values of the radical group of chemicals (species characterized by very rapid rates of change; appear in 'fast' reactions) were found to be unimportant to later results. Unlike earlier studies using sensitivity coefficients it was noted that the behaviour of the radicals during the interval of integration can have a profound effect on the outcome of the simulation. Straightforward applications of the Taylor series expansion can therefore yield grossly inaccurate results. To overcome this difficulty, the radicals and their effects were modelled using the pseudo steady-state approximation, in which the rates of change of the radicals are set to zero and their concentrations result from the solution of a set of non-linear equations.

Initial tests of the Taylor series as a means of integration confirmed Dunker's (1986) results; Taylor series integrations required between two and three orders of magnitude less processing time than the equivalent Gear integrations. Tests in which the two integration methods were compared over several time steps showed results of comparable accuracy. Tests of the method using the pseudo steady-state approximation are currently underway.

AP12

INTRODUCTION

The deleterious effects of increasing concentrations of acidic air pollutants, especially SO_2 and NO_x, have become increasingly apparent particularly in eastern North America and northern European countries. Although stemming from a variety of sources a substantial contribution to the problem arises from the sometimes high concentrations of pollutants in flue gas discharges from industrial smelting and coal refining. One of the aims of this study is to examine the applicability of a technique involving specific, rapid heating of certain catalytic surfaces by microwave energy as a method for destruction of acidic air pollutants.

EXPERIMENTAL

The technique involves exposing a catalyst bed through which the reagent gases are flowing to short, high intensity "pulses" of microwave irradiation. The catalysts chosen are selected for their strong interaction with microwaves as well as for their chemical interactions with the gaseous reagents and products. As a result of the highly lossy nature of the catalysts the incident microwave energy is rapidly and efficiently converted to high surface temperatures. This initiates chemical reactions of adsorbed gases even though they themselves are essentially transparent to microwave irradiation.

For the purposes of preliminary experiments a simple commercial microwave oven was modified to allow assessment of the potential of the method over a variety of different catalysts. The experimental set-up can be described as shown in the scheme below. A timing device was installed to permit a variety of on/off duty cycles of the magnetron. Concentrations of SO_2 or NO in excess of those generally found in flue gas effluents were used in most of the experiments as it was felt that in general the results would be applicable to more dilute systems as well. Both commercially available (proprietary) and metal powder catalysts have been used. Detection of products was by on-line gc.

DISCUSSION

For SO_2 experiments typically 5% SO_2 in air was irradiated as it flowed through the catalyst bed. Removal of >98% of the SO_2 for prolongued periods of time was possible using a variety of catalysts, especially several containing substantial Ni/NiO concentrations. Of principal interest to us were those reactions which appeared to result in reduction of the SO_2 giving O_2 and either S_x or metal sulfides as products. Verification that the O_2 came from the SO_2 could be demonstrated in experiments using SO_2/He mixtures over catalysts previously deoxygenated by various methods.

In addition experiments using aqueous slurries of metal powders were found to give positive results. Ni, Cu, and Fe powders alone were inactive in destruction of SO_2, however, aqueous slurries of these metals gave removals of >60% of the SO_2 (for the Fe powder), and the production of O_2 and FeS/S_x. The conversion of SO_2 to either metal sulfides or to possibly recoverable sulfur is economically extremely desireable, as well as avoiding the disadvantages of dealing with corrosive oxidized acidic products typically produced in SO_2 removals.

Removal of NO (typically 25% in He) was also examined. Several commercial copper containing catalysts sold for NO_x removal were inactive in our experiments. However, some Ni-containing commercial catalysts as well as in-house Ni/graphite pellets demonstated removal of NO to levels undectable by gc for long periods of time. The products detected included N_2, O_2, CO and CO_2 and at long experimental times N_2O. Some problems were evidenced in that the catalysts tended to become oxidized and could not be easily regenerated and reused. Further experiments using a variety of different fuels in the feed gas, including methane, NH_3, and H_2O are underway. Initial results appear promising in that substantial increases in catalyst lifetime without minimising

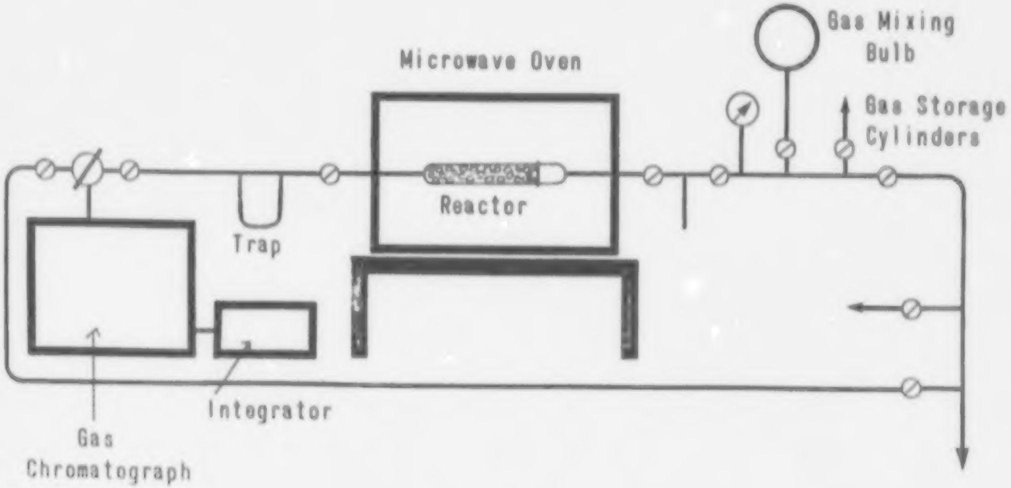
NO destruction are realized.

Expansion of the project to include studies of polyaromatic and halogenated hydrocarbon pollutants is planned and is commencing. In addition we plan to examine more realistic mixtures of flue gas effluents to determine the effects of mixtures of components once the optimum type of catalyst has been determined.

ACKNOWLEGMENT

The support of the Ontario Ministry of the Environment is gratefully acknowleged.

Figure 1


Microwave Oven
Reactor
Gas Mixing Bulb
Gas Storage Cylinders
Trap
Integrator
Gas Chromatograph

AP13

AN INVESTIGATION OF VIBRATION ISOLATION IN A HOUSE FOR REDUCTION OF TRAIN VIBRATIONS, PART 1: EVALUATION OF TRANSDUCER MOUNTING IN THE GROUND,

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INTRODUCTION

The measurement of ground-borne vibrations from sources such as railway and highway traffic constitutes an important part of investigations of the effects of these vibrations on nearby houses. Consequently it is important to ensure that these measurements are undistorted and accurate. In this respect, the complexity and difficulty of proper transducer attachment to the ground is known to be a major obstacle. Measurement transducers, which are generally very small in size, are mounted on larger objects, e.g. a stake or a plate, which may provide sufficient coupling to the ground. However, proper coupling to the ground may not always be achieved; kinematic and inertial effects occur due to the geometry and mass of the mounting device, respectively. Consequently the measurement system supported by the ground will form a resonant system that may not faithfully transmit the free field motion to the transducer.

The present study is the first part of a 3-part investigation into vibration isolation methods of houses for train vibrations. Parts 2 concerns the characteristics of train vibrations in the ground and Part 3 deals with the performance of a vibration isolation system in a test house. These are currently in progress and results will be reported separately at a later date.

OBJECTIVE

The objective of this study (part 1) is to make a comparative assessment of the performance of different methods of mounting transducers in the ground and to determine the frequency range over which accurate measurement of the ground motion can be expected. Initially, a literature survey was carried out, as a result of which three transducer mounting methods were chosen for further investigation and tested according to unified procedures:

- transducer mounted on a spike driven into soil
- transducer mounted on a plate attached to the ground with thin nails
- transducer mounted in a box, of density equivalent to that of soil, embedded in the ground.

The performance of these mountings was evaluated by subjecting them to frequency response tests, from which an assessment of measurement errors can be made.

TESTING METHOD

In the frequency response test the mounting system is excited using two methods:

- applying an impact to the mounting separately in the horizontal and vertical directions with a small instrumented hammer;
- coupling an electrodynamic exciter to the mounting. The excitation is band limited white noise.

Fourier transforms of the force and acceleration were then computed and the results displayed in one of two forms: acceleration divided by force (i.e.

acceleration frequency response); or, after double integration, displacement divided by force (i.e. displacement frequency response).

Tests were carried out in a laboratory soil box proved unsuitable and therefore all further tests were carried out at two exterior sites in natural ground. The soil type at the first site is stiff clay and that at the other site is fine sand. Calibration tests indicated that virtually the same frequency response of the mounting system could be obtained with either of the two excitation methods. Thus the hammer was subsequently used for most of the tests reported since it was found more convenient to use in a field environment.

RESULTS

The accurate frequency range of measurements is that over which the displacement response is constant (or flat), as illustrated in Figure 1a. A constant displacement frequency response implies negligible inertial effects of the mounting. The part of the displacement response curve which is flat corresponds to a part of the acceleration response curve which is parabolic, as can be seen from Figure 1b. Expressing the acceleration amplitude in decibels (dB), the acceleration response function is then equal to $10 \log (D_0 \omega^2)^2 = 40 \log (\omega) + 20 \log (D_0)$, where D_0 is the constant displacement amplitude, and ω is the frequency. Hence, by alternatively considering the acceleration response curve of the system, the frequency range for which accurate measurements can be expected is that over which the response curve is sloping at 40 dB/decade, as shown in Figure 1c.

Table 1: Upper frequency limits (Hz) of the acceptable measurement range to within ±3 dB amplitude tolerance

Site	Direction	175x175 mm Wood Plate With Rods	90x90 mm Wood Plate With Rods	300 mm long spike	150 mm long spike	Embedded Box
1	Vertical	350	720	-	482	322
	Horizontal	278	415	-	322	401
2	Vertical	255	330	759	442	122
	Horizontal	235	209	643	311	208

The upper limit of this acceptable frequency range is chosen as the frequency at which the response curve first deviates from the 40 dB/decade slope by ± 3 dB. On a linear scale, this corresponds to an error tolerance of 41%. These frequency limits for the ± 3 dB acceptable measurement range are summarized in Table 1. Finally, simultaneous measurement of the ground motion induced by a moving train using the three mountings located side by side produced comparable amplitude Fourier spectra.

CONCLUSION

The frequency response characteristics of the tested mounting designs found in this study show that adequate accuracy of ground vibration measurements up to about 100 Hz can be achieved for the typical soils of sites 1 and 2. However, when these mountings are attached to weaker soils, the maximum frequency of the acceptable frequency range will be lower than that of the test sites in this study. If the reliability of a mounting system for a specific soil is suspect, a frequency response test should be performed at the site in question to verify the acceptable measurement range.

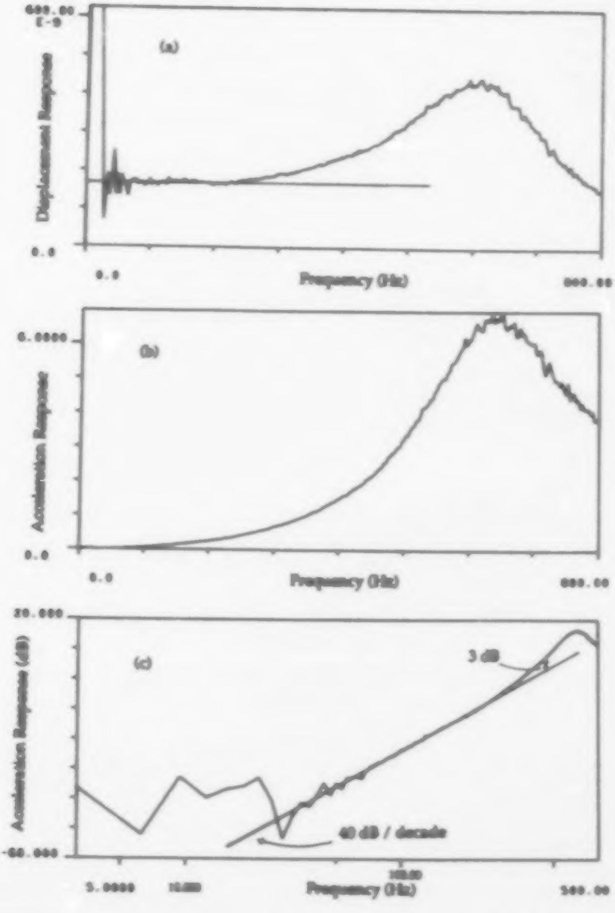

Figure 1 Frequency response curves of wood plate attached to soil with threaded thin rods: a) displacement response, b) acceleration response (linear scale), c) acceleration response (decibels).

AP14

ADAPTATION OF A MESOSCALE ATMOSPHERIC MODEL TO STUDIES OF AIR POLLUTION IN THE TORONTO AREA

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1. Introduction

Numerical models of transport, transformation and deposition of atmospheric pollutants require adequate knowledge of meteorological conditions in the area of simulation. Depending of the model, the meteorological data required may include three-dimensional fields of wind velocity (including its vertical component) as well as temperature, humidity, clouds and precipitation, turbulence parameters etc. This meteorological information can be either taken from observations, produced by an outer meteorological model or generated by an internal module of the pollution model. For example, ADOM, the Acid Deposition and Oxidant Model (Venkatram et al., 1988) uses meteorological fields provided by the large scale NWP model from the Canadian Meteorological Centre and combines them with the output of a boundary layer model (Scholtz et al., 1986).

The mesoscale or urban scale pollution models require however meteorological fields with resolution of the order of several km which are not readily available. The only feasible way to provide such high resolution fields is by means of a mesoscale atmospheric model. This paper describes such a model and discusses its implementation for the Toronto area and the principles of its use for the pollution studies.

2. The Gesima model

Gesima (GEesthacht SImulation Model of the Atmosphere) is a sophisticated, mesoscale model developed at the GKSS Forschungszentrum in Geesthacht, West Germany. The model solves the non-hydrostatic, anelastic equations of motion in terrain-following coordinates using the MacCormack scheme (for details on dynamics and numerics of Gesima see Kapitza, 1987). The turbulent diffusion is parameterized according to the mixing length approach. A sophisticated surface layer module is used for computing the heat and moisture balance at the ground level, taking into account the shortwave and longwave radiation, heat and moisture fluxes in soil etc. The model includes also a cloud module computing mixing ratio of cloud water, rain and cloud ice/snow (combined in one variable) using the 'bulk microphysics' approach.

The model can be used for pollution studies either by development of a special module for the transport, transformations and deposition of pollutants, or by using its output for an external pollution model like ADOM. A chemical module implemented in Gesima by the author is described in the following section. A run of Gesima simulating the evolution of atmospheric fields during a period of the OSCAR experiment in the Toronto area is currently being prepared. Its results are intended as fine resolution input fields for ADOM which could then be used for mesoscale simulations. The details of this run are given in section 4.

3. The chemical module of Gesima

Passive transport and turbulent diffusion of pollutants are treated in Gesima similarly as those of other components like humidity, cloud water etc. (advection terms are computed according to the Smolarkiewicz scheme). During his two visits in GKSS, in 1988 and 1989, the author implemented in Gesima a chemical module simulating scavenging and chemical transformations of acid rain producing pollutants, developed originally at the University of Toronto and the Ontario Hydro (Cho et al., 1989), based on the approach of Iribarne and Cho (1989). Main modifications of the original model included adapting it to the microphysical parameterizations of Gesima as well as the vectorization of the code. Subroutines computing budgets of chemical variables have also been developed.

The model simulates oxidation of SO_2 in cloud and rain water by H_2O_2 and O_3, oxidation of NO_x in gaseous phase with subsequent dissolution in cloud water of the HNO_3 and HNO_2 formed, as well as transfers of chemical species between various classes of hydrometeors due to microphysical processes (autoconversion, accretion, freezing, melting etc.) and their deposition at the ground.

Results of some simulations with this module (but implemented in an early, hydrostatic version of Gesima) are described by Niewiadomski et al. (1989).

4. Gesima run for the Toronto area

In order to provide the input meteorological fields for fine resolution simulations with ADOM, a Gesima run is being prepared for the Toronto area. The domain of simulation will cover one regular grid cell of ADOM (127 x 127 km) with Toronto located in its SE quarter. The final horizontal grid sizes and the time step of simulation will be chosen after completion of the current tests of the model, but will probably not exceede 5 km and 30 s respectively. Vertical structure of the grid will correspond to that of ADOM, with 12 levels.

Since the available topography data have 5 km resolution, with a grid not necessarily corresponding to that of Gesima, a subroutine interpolating from those data elevation of each grid cell of Gesima, independent of the model resolution has been developed. Similarly, the surface parameters like heat capacity, emmissivity, albedo, roughness length, field capacity etc.) are determined according to the percentages of different types of land use in each grid cell, interpolated from an EPA data base having resolution of 0.25 deg longitude and 0.166 deg latitude.

The initial and boundary meteorological conditions come from the April 21 - 24, 1981 case of the OSCAR experiment, for which extensive air pollution and precipitation chemistry data are available. The described in this section simulations with Gesima are expected to complete by the end of 1989. The three-dimensional fields of wind velocity, temperature, humidity, hydrometeors etc. will be stored in appropriate intervals on magnetic tape to allow future mesoscale simulations with ADOM or other mesoscale pollution models.

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VOLUME I
SESSION B
WATER QUALITY RESEARCH
VERBAL PRESENTATIONS

B2

ORGANIC CONTAMINANTS IN FOOD WEBS: MECHANISMS, MODELS AND MANAGEMENT

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INTRODUCTION

Research at the Great Lakes Institute of the University of Windsor is directed to assist government and industry in the environmental management of contaminants. This includes activities such as

(i) Modelling of chemical movement in the Great Lakes and in the Great Lakes aquatic food-chain. The purpose of this modelling effort is to establish a reliable link between source and chemical impact.

(ii) Providing technical information regarding the chemical dynamics in individual organisms and in food-chains, which is required for the development of guidelines.

(iii) Providing tools and protocols for monitoring of contaminants in the Great Lakes.

To accomplish these objectives a research program has been developed that consists of the following components:

(i) Laboratory studies, focusing on specific mechanistic aspects of chemical dynamics.

(ii) Field studies, testing and validating laboratory findings under field conditions.

(iii) Computer modelling, which enables calculations involving the complexities encountered in the field, and which provides an up-to-date knowledge-base in an accessible and applicable form.

To illustrate our research strategy, we present a summary of our studies of the chemical dynamics in aquatic macrophytes, in particular Myriophyllum spicatum. The main objective of this report is to demonstrate how we integrate laboratory studies, field studies and food-chain/ecosystem modelling.

DEVELOPING A DESCRIPTIVE MODEL

Figure 1 illustrates the results of a typical experiment, investigating the chemical dynamics in a macrophyte species, i.e. the uptake of hexachlorobenzene (HCB) in Myriophyllum spicatum as a result of aqueous exposure. After the plants were transferred to clean, uncontaminated water, a loss of the chemical from the plants was observed with time. This is illustrated in Figure 2. During the first 37 days, the concentration of all chemicals in the plants dropped logarithmically with time, which is illustrated by the linear decrease of log C_p with time. During the remainder of the elimination period, the decrease of C_p tends to be somewhat slower than during the first 37 d, causing a deviation of the initial linear drop of log C_p with time.

The observed uptake of the test chemicals from the water by the plants, followed by the decrease of the chemical concentration in the plant after the plants are transferred to clean water, suggests that the chemical uptake in the plants is a reversible process. The simplest description of this process is

$$C_p \rightleftharpoons C_w \qquad (1)$$

This model describes distribution of the chemical between two compartments i.e. the plants and the water, which are both considered to be homogeneous. Chemical transfer from the water to the plant is represented by a rate constant k_1, which has units of reciprocal time (d^{-1}). Chemical transfer from the plant to the water is characterized by a rate constant k_2 with units of d^{-1}. The following differential equation describes the net flux of chemical F_p (mole chemical/time) between the water and the plant:

$$F_p = d(V_p.C_p)/dt = k_1.V_p.C_w - k_2.V_p.C_p \qquad (2)$$

where $k_1.V_p.C_w$ or is the flux from the water into the plant, i.e. F_1 (mol/s) and $k_2.V_p.C_p$ is the flux F_2 (mol/s) from the plant to the water. To derive the relationship between the chemical concentration in the water and that in the plant, equation 2 should be integrated. This can be performed simply when the chemical concentration in the water, as well as the volume (or weight) of the plant and the rate constants for uptake and elimination are constant with time (i.e. no growth), resulting in

$$C_p = C_w.(k_1/k_2).\{1 - \exp(-k_2.t)\} \qquad (3)$$

From equation 3 it transpires that, when exposed to a constant chemical concentration in the water, the chemical concentration in the plant increases logarithmically with time and then approaches a constant level i.e. $C_w.(k_1/k_2)$. The ratio of the uptake and elimination rate constants, i.e. (k_1/k_2), can thus be referred to as the plant-water bioconcentration factor K_{pw}.
Integration of equation 1 can also be achieved when the chemical concentration in the water is zero, such as during a typical depuration experiment when contaminated plants are exposed to clean water. Under those conditions integration of equation 1 gives

$$C_p = C_{p,t=0}.\exp(-k_2.t) \qquad (4)$$

or

$$\log C_p = \log C_{p,t=0} - k_2.t \qquad (5)$$

where $C_{p,t=0}$ is the concentration in the plant at the beginning of the depuration period. Equation 4 demonstrates that the plant-water exchange model predicts an exponential decrease of the C_p with time during the depuration experiment.

The applicability of the reversible plant-water exchange model can be determined by fitting the model to the experimental data. This could have been simply

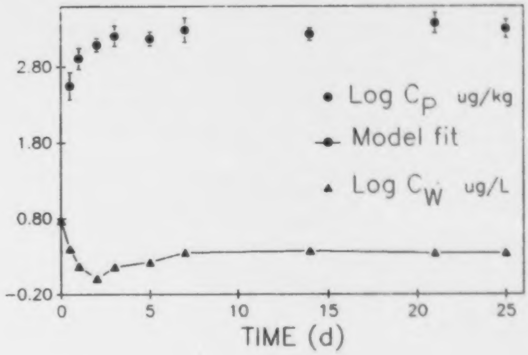

Figure 1 : Logarithms of the concentrations of hexachlorobenzene in the water, C_w (ug/L), and in the plant C_w (ug/Kg) during the uptake experiment. The solid line illustrates the model fit.

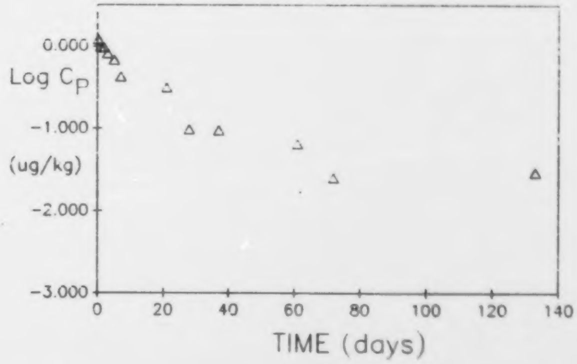

Figure 2 : The logarithm of the chemical concentrations in the plant C_p (ug/Kg) during the elimination experiment.

achieved by fitting the observed increase of C_p with time to equation 2. However, this is only correct if during the experiment the chemical concentration in the water was constant and plant growth was insignificant. Plant growth, on a weight basis, was less than 5% over the 25 d uptake phase, and thus considered to be insignificant. But Figure 1 clearly demonstrates the variation of the chemical concentration in the water with time. The model was therefore fitted to the experimental data by a numerical integration procedure. This procedure derives the chemical concentration in the plant as the sum of increments in plant concentrations dC_p over time intervals dt, i.e. $C_p = \sum dC_p$
Each dC_p is calculated from equation 1, i.e.:

$$dC_p = (k_1.C_w - k_2.C_p).dt \qquad (6)$$

where (i) dt was chosen to be sufficiently small, (ii) C_w at every exposure time t, followed from water concentration measurements by fitting the observed water concentrations to a series of linear functions, which each connect the observed water concentration data at two consecutive exposure times, and (iii) k_1 and k_2 were selected to produce the best agreement between calculated and observed C_p. The best fit of the observed data was the one with the k_1 and k_2 value, for which the sum of the squared differences between calculated and observed C_p was the smallest. For hexachlorobenzene k_1 was 150 d^{-1} and k_2 was 0.14 d^{-1}. The quality of the fit can be expressed by the normalized deviation, E, of the predicted (i.e. model) from the observed values

$$E = \sqrt{(C_p^O - C_p^M)^2/n} \qquad (7)$$

where C_p^O is the observed, and C_p^M is the predicted concentration in the plant and n is the number of observations. In this fashion it was estimated that for hexachlorobenzene, the observed and fitted plant concentrations vary, on average, only by 15%. This is well within the range of experimental error associated with plant and water analysis. In general, the deviation between observed and fitted plant concentrations ranged from 10 % to 45%. This demonstrates that the model agrees well with the experimental data.

Figure 2 demonstrates that the decrease of the concentration in the plant during the first 40 d of the elimination period is in agreement with the exponential drop of C_p (equation 4 and 5) predicted by the reversible plant-water exchange model. The rate constant for chemical elimination was thus determined from the slope of the log C_p-time plots, i.e. k_2 is 0.069 d^{-1}. After the first 40 d of the elimination period, the decrease of the chemical concentration in the plant tends to be somewhat slower. This does not agree with the plant-water two compartment model. It could indicate that a small fraction of the chemical in the plant is less accessible than the majority of the chemical. However, it may also be due to experimental error associated with the long exposure times.

The two independent measurements of k_2 (i.e. from uptake and elimination data) are in reasonable agreement. But, in general, the elimination rate constants derived from the elimination experiment (i.e. k_2) are approximately half of those derived from the uptake experiment (i.e. k_2^*). This discrepancy may be due to the fact that k_2 was derived from data over a 40 d period, while k_2^* was derived from data over a 25 d period. It is possible that when fitting data over the longer 40 d period, the influence of the relatively slow chemical transfer rate into less accessible plant compartments on the overall elimination rate is larger than when fitting over a shorter 25 d period. This could result in k_2 being somewhat lower than k_2^*.

Now that the uptake and elimination rate constants have been determined, it is possible to derive the bioconcentration factor of HCB, K_{pw}, in the plant as

$$K_{pw} = k_1/k_2^* \qquad (8)$$

The bioconcentration factor of HCB was thus determined to be 1,072. When expressed on a lipid weight basis as K_{lw}, i.e. the ratio of chemical concentration in plant lipids over that in the water, the bioconcentration factor of HCB is 537,000 i.e. approximately similar to its K_{ow} of 295,000. This suggests that chemical bioconcentration in the plant is essentially a chemical partitioning process which can be mimiced by 1-octanol-water partitioning. This indicates that the chemical's affinity for the actual storage site in the plant is similar to that for 1-octanol. It also indicates that bioconcentration of the investigated chemicals in the plant is a thermodynamically controlled process, determined by the affinity of the chemical for the plant relative to that for water. It thus appears that uptake and elimination of HCB are passive processes, controlled by a thermodynamic gradient, and that there is no active transport.

DEVELOPING A MECHANISTIC MODEL

To develop a mechanistic model for chemical uptake and depuration in the plant, it is preferable to have uptake and elimination data for a larger number of chemicals. This is done and preliminary data are presented in Figure 3 and 4. In Figure 3 the uptake rate constant is plotted versus the 1-octanol-water partition coefficient. It illustrates that for chemicals with log K_{ow} below 6.5, k_1 increases with increasing K_{ow}, while for the chemicals with log K_{ow} exceeding 6.5, k_1 tends to approach a constant value of 500 d^{-1}. In Figure 4, k_2 is plotted versus K_{ow}. It shows that with increasing K_{ow}, k_2 drops, first slowly, but then more profoundly.

To explain this "biphasic" nature of the rate constant's relationship with K_{ow}, we propose a simple mechanism, which is based on the assumption that chemical bioconcentration in the plant involves chemical permeation through aqueous and organic parts of the plant. Examples of organic phases in the plants are the lipid bilayers of biological membranes or the plant's cuticle. Aqueous phases are present in several forms, for example, associated with membranes. In absence of active transfer mechanisms, transport of chemical from the ambient water to the storage site involves either simple molecular diffusion, movement through natural fluid flow in the plant, or both. When transport involves molecular diffusion, the chemical flux can be expressed by

$$F = k.A.\Delta C \qquad (9)$$

where k is the mass transfer coefficient (m/s), A is the area of diffusion (m^2) and C is the concentration gradient (mol/m^3). If transport is by fluid flow, the flux is

$$F = Q.\Delta C \qquad (10)$$

where Q is the fluid flow (m^3/s). If both diffusion and fluid flow are involved

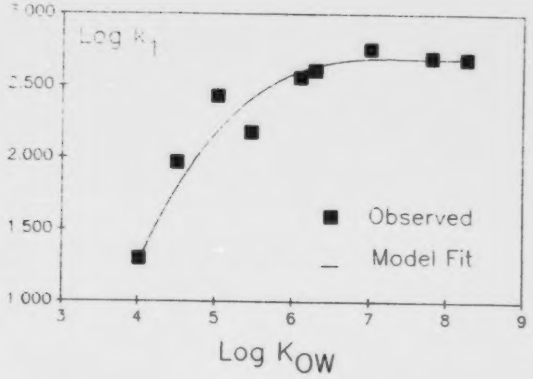

Figure 3 : The logarithm of the uptake rate constant, log k_1 (d^{-1}), in the plant and the logarithm of the 1-octanol-water partition coefficient, log K_{ow}. The solid line represents the model fit.

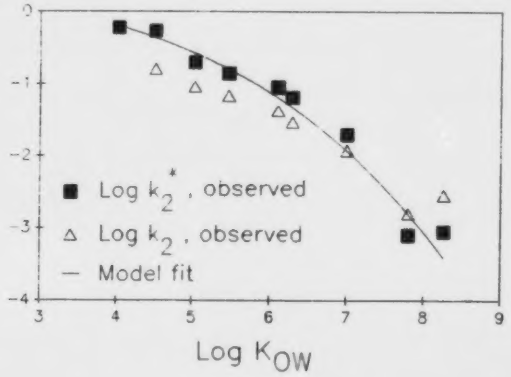

Figure 4 : The logarithm of the elimination rate constant, log k_2 (d^{-1}), in the plant and the logarithm of the 1-octanol-water partition coefficient, log K_{ow}. The solid line illustrates the model fit.

in the transport process, it is possible to express the chemical flux as

$$F = D.\Delta C \qquad (11)$$

where D is the sum of all possible diffusion and fluid flow processes combined, i.e. D equals

$$D = \sum(k_i.A_i) + \sum Q_j \qquad (12)$$

D can be viewed as the chemical's conductivity, and its reciprocal, i.e. 1/D, as a resistance R (d). Since our experiment is not able to identify the mode of transport, i.e. diffusion, fluid flow, or both, involved in the bioconcentration process, we will refer to equations 11 and 12 as the best representation of the chemical flux. The chemical flux in aqueous phases of the plant, F_W (mol/s), is thus expressed as

$$F_W = D_W.\Delta C_W \qquad (13)$$

where D_W (m^3/s) is the chemical's conductivity in the water phases of the plant. The flux in the organic phases of the plant, F_L (mol/s), can be expressed as

$$F_L = D_L.\Delta C_L \qquad (14)$$

where D_L (m^3/s) is the chemical's conductivity and C_L (mol/m^3) is the chemical's concentration in the organic phases of the plant.

In general, the solubility of organic substances in the organic phases of the plant are higher than that in the aqueous phases. The organic phase thus has a larger capacity to accommodate organic substances than the water. This difference is expressed by the chemical's organic phase/water partition coefficient K_{LW}, i.e. C_L/C_W. It thus transpires that at all times the organic phase can transport a larger amount of chemical than the aqueous phase. This can be illustrated by expressing F_L in terms of C_W, i.e.

$$F_L = D_L.K_{LW}.\Delta C_W \qquad (15)$$

The overall chemical flux from the water into the plant, F_1 (mol/s), can be expressed as

$$F_1 = D_P.C_W \qquad (16)$$

where D_P (m^3/s) is the chemical's overall conductivity in the plant. If chemical transport in organic and aqueous phases occur in series, it follows that the total resistance for chemical uptake in the plant, R_P (i.e. $1/D_P$) is equal to the sum of the resistances in the aqueous, R_W (i.e. $1/D_W$) and in the organic phases, R_L (i.e. $1/D_L$):

$$R_P = 1/D_P = R_W + R_L/K_{LW} = 1/D_W + 1/D_L.K_{LW} \qquad (17)$$

Substitution of equation 17 into equation 16, and replacing F_1 by $k_1.V_P.C_W$ illustrates that k_1 can be expressed in terms of the aqueous and organic phase conductivities in the plant as:

$$1/k_1 = V_P/D_W + V_P/D_L.K_{LW} \qquad (18)$$

In a similar fashion, k_2 can be expressed in terms of the aqueous and organic phase resistances. First, equation 17 is substituted in the equation for the overall chemical flux F_2 from the plant to the water, i.e.

$$F_2 = D_p.C_p/K_{pw} = D_p.C_p/(L_p.K_{lw}) \quad (19)$$

where K_{pw} is the bioconcentration factor in the plant, which, as was shown earlier, appears to be satisfactorily represented by the chemical's partition coefficient between plant lipids and water K_{lw} or by K_{ow}. If F_2 is then replaced by $k_2.V_p.C_p$, it follows that:

$$1/k_2 = L_p.V_p(K_{lw}/D_w + 1/D_l) \quad (20)$$

If K_{lw} in equations 18 and 20 are replaced by K_{ow}, it follows that

$$1/k_1 = V_p/D_w + V_p/D_l.K_{ow} \quad (21)$$

$$1/k_2 = L_p.V_p(K_{ow}/D_w + 1/D_l) \quad (22)$$

Equations 21 and 22 demonstrate that when chemical exchange between the plant and the water involves aqueous and organic phases in series (e.g. membrane permeation), the kinetics of uptake and elimination tend to be controlled by transport in the organic phases when the chemical's K_{ow} is low. With increasing K_{ow}, transport processes in the aqueous phases of the plant become more important and ultimately dominate the kinetics. This is reflected by (i) a k_1 which increases with increasing K_{ow} and then approaches a constant level (i.e. D_w/V_p) for high K_{ow}, and (ii) a k_2 which tends to be approximately constant (i.e. $D_l/V_p.L_p$) for low K_{ow} chemicals and then drops with increasing K_{ow}.
The applicability of this mechanistic model is demonstrated by its fit to our experimental data, resulting in :

$$1/k_1 = 0.0020 + 500/K_{ow} \quad (23)$$

$$1/k_2^* = 1.58 + 0.000015.K_{ow} \quad (24)$$

The quality of the fit is illustrated in Figure 3 and 4. The good agreement between model and experimental data, provides the opportunity to estimate D_w/V_p and D_l/V_p. Comparison of equations 21 and 23, shows that D_w/V_p is 500 d and D_l/V_p is 0.0020 d. From equations 22 and 24, it follows that D_w/V_p is 133 d and D_l/V_p is 0.0013 d.

It is now interesting to discuss the significance of our findings in terms of a chemical transfer mechanism(s) in aquatic plants. Studies of the uptake of carbondioxide and the release of oxygen indicate that simple passive diffusion is the predominant mode of transport. Our study also indicates that there is no active transport mechanism for the investigated organic substances. It is thus conceivable that chemical uptake and elimination in the plant is also the result of passive molecular diffusion. If diffusion is indeed the transport mechanism for chemical uptake and elimination, then D_w is $k_w.A$ and D_l is $k_l.A$, where k_w and k_l are the mass transfer coefficients in respectively the aqueous and organic phases of the plant and A is the diffusion area. It then follows that D_w is $k_w.A/V_p$ and D_l is $k_l.A/V_p$. Since our data indicate that D_w/V_p is between 133 and 500 d and that D_l/V_p is between 0.0013 and 0.0020 d, it is possible estimate k_w and k_l if the diffusion area per volume plant (i.e. A/V_p) can be determined.

Measurements of the actual diffusion area may be difficult. But it may be possible to estimate the diffusion area/volume ratio relationship. This may render the aqueous and organic phase mass transfer coefficients, which may be too different among various macrophyte species. It may thus be possible to estimate the rate constants of chemical uptake and depuration in aquatic plants from the area/volume ratio of the plant. It is obvious that this is an hypothesis rather than a finding. Further research is required to demonstrate if there is sufficient basis that would allow rate constants of chemicals in aquatic macrophytes to be estimated from the area/volume ratio of the plant and the K_{ow} of the chemical.

MODELLING

Now that we have developed a basic understanding of chemical dynamics in aquatic macrophytes, it is interesting to investigate the influence of plants on the chemical dynamics in a complete ecosystem. For example, it may be possible that the plant is consumed by another organisms, thus introducing the chemicals in the plant into the food-chain. And when the plants are not consumed, they may affect the chemical concentration in the water, because of their sorptive capacity and their abundance.

In order to do this, it is important to view the chemical dynamics in a particular organism in an ecosystem sense. We then have to consider a variety of factors other than those examined in individual laboratory experiments. For example, growth, lipid, feeding rates, predator-prey relationships, temperature, oxygen levels, metabolic activity, bioavailability, sediment-water interactions etc. The effect of some of these factors are known, the effect of other are yet unknown. Under field conditions, all of these factors vary with time, depending on season and temperature. Some of these factors may have profound effects on chemical body burdens in organisms, others may not have a significant effect.

Since it virtually impossible to estimate the overall-effect on the body burden of an organism, we have developed a food-chain model ECOTOX (Gobas, 1989) which puts all possible processes affecting the chemical body burden in proper perspective. ECOTOX is a computer model which predicts the body burden of organic chemicals in different compartments of the aquatic food-chain and resulting acute and chronic toxic effects, based on time-dependent input information of chemical concentrations in water and sediments. The model is dynamic i.e. it does not rely on steady-state or equilibrium assumptions. It makes it particularly useful for spill events, which are characterized by unusual changes in environmental conditions. The model incorporates equations for chemical uptake and elimination in fish, algae and benthic invertebrates. These equations are the result of experimental work in the laboratory and in the field. The model thus provides the framework, into which new scientific research can be incorporated.

The model involves the following variables: K_{ow} of the chemical, the body weights of 4 species of fish, lipid content, growth rate, feeding rate, tropho-dynamics (i.e. predator-prey relationships), temperature, oxygen content of the water, concentration organic matter in the water, organic carbon fraction of the sediment. If available, information regarding these variables and their variation with time can be simple incorporated in the model. If not available, ECOTOX will assume typical values for most (but not all, e.g. K_{ow}) of the variables. It is obvious that with more specific knowledge of the local environmental conditions and the biology of the ecosystem predictions of chemical body burdens and toxic effects can be more reliable. The model is particularly useful for the assessment of the effects of spills and chemical discharges on a specific organism which is of particular ecological or economic importance. With specific information regarding the characteristics of this organism

We believe that with continued effort exploring mechanisms of chemical dynamics, validating or testing laboratory findings in the field, and presenting our knowledge in an accessible and usable form, we can continue to support the Ministry with the tools required for environmental management of contaminants in the Great Lakes and elsewhere in the province.

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B3

ORGANOCHLORINE CONTAMINANT BURDENS OF ADULT AQUATIC INSECTS COLLECTED FROM GREAT LAKES CONNECTING CHANNELS

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Ontario Ministry of the Environment
Technology Transfer Conference
Toronto, Ontario
November, 1989

ABSTRACT

Adult Trichoptera and Ephemeroptera are potentially useful indicators of contamination in aquatic systems because their larvae accumulate significant organochlorine (OC) contaminant burdens from the sediment in which they live. We employed light traps to capture adult Trichoptera at up to 5 stations along each of the Detroit, St. Clair, Niagara, and St. Marys rivers, and compared the insects' OC contaminant burdens with the amount and type of reported sediment contamination in these rivers. Detroit River Hydropsychidae contained highest concentrations of PCBs, while levels of QCB (pentachlorobenzene), HCB (hexachlorobenzene), and OCS (octachlorostyrene) were greatest in St. Clair River animals, relative to all rivers sampled. Contaminant concentrations in insects collected simultaneously on the U.S. and Canadian banks of the Detroit River at Detroit/ Windsor were consistent with local sediment contamination. Niagara River caddisflies contained elevated levels of PCBs. Lower Niagara River Leptoceridae were less contaminated by pesticides than Hydropsychidae from the upper Niagara. Samples of Trichoptera from the St. Marys River were small, diverse, and relatively uncontaminated. Spatial trends were also observed within rivers. Temporal variation was unpredictable in contaminant burdens of Detroit and St. Clair river Hydropsychidae. Overall, insect contaminant burdens corresponded well with literature reports of sediment contamination.

1. INTRODUCTION

Recent research has addressed the potential importance of benthic invertebrates as agents of contaminant transfer between sediments and higher trophic levels in aquatic systems (Larsson 1984, Oliver 1984, Pugsley et al. 1985, Reynoldson 1987, van der Oost et al. 1988). Benthic invertebrates, relatively sedentary organisms, tend to bioaccumulate compounds such that contaminants detected in the tissues of organisms collected in a particular area can be ascribed to sediment contamination in the region of collection (Reynoldson, 1987).

Adult insects that have emerged from aquatic habitats have great potential as a biomonitoring tool and provide a cost effective alternative to sampling organisms directly within the aquatic environment. Caddisflies (Trichoptera) and mayflies (Ephemeroptera) spend most of their life as larvae, within or in contact with the sediments. The night-active, winged adults emerge during the summer in large numbers. Adults are shortlived, typically do not feed or defecate, and with the exception of a small proportion of contaminants shed with the larval skin (Larsson 1984), body burdens remain unchanged following emergence.

Great Lakes connecting channels (Detroit, St. Clair, Niagara and St. Marys) support large populations of aquatic insects. These rivers have been designated "Areas of Concern" due to long term inputs of pollutants, resulting in the presence of various types of contaminants (OC contaminants and heavy metals) in the sediments (International Joint Commission 1985). Adults of aquatic insects inhabiting these large rivers can be easily captured using light traps (Kovats and Ciborowski 1989). These animals have been successfully used as indicators of sediment contamination by Mauck and Olson (1977), Clements and Kawatski (1984), Ciborowski and Corkum (1988), and Kovats and Ciborowski (1989). Reported adult insect OC contaminant body burdens corresponded broadly to local sediment concentrations at each lake or river sampled by these workers. Our goal during this study was to compare the amount and type of OC contamination among adult aquatic insect samples collected by standardized methods the connecting. Our specific objectives were the following:

1. To compare contaminant body burdens of adult aquatic insects to reported sediment concentrations;

2. To determine if contaminant burdens of adult insects vary among Great Lakes connecting channels;

3. To study temporal variation in contaminant burden during the emergence season of aquatic insects.

2. MATERIALS AND METHODS

2.1. Sample collection

Light trap collections were made at up to five stations along each of the connecting channels in 1988, using procedures developed by Kovats and Ciborowski (1989). Light trap samples were collected at two sites (upstream and downstream) along each of the Detroit and St. Clair rivers (Table 1), once during each of June, July, and August. Single visit collections were made at five sites on the Niagara River (5-6 July), and four locations on the St. Marys River (28-30 June and 15-17 Aug.; Table 2).

Table 1. Locations of stations sampled during the seasonal variation study.

Stn	River or Lake	Designation	Latitude (North)	Longitude (West)
1	Detroit R.	River Canard	42°11'48"	83°06'13"
2	Detroit R.	East Windsor	42°20'27"	82°56'56"
3	St. Clair R.	Sombra	42°42'02"	82°29'03"
4	St. Clair R.	Sarnia	42°54'12"	82°27'29"

To evaluate smaller-scale spatial variation in body burdens of adult aquatic insects, we performed simultaneous trapping on the north and south banks of the Detroit River, downstream from Lake St. Clair (8 July, 1988). This study was conducted in collaboration with Dr. Mary Henry, (U.S. Fish and Wildlife Co-op, University of Minnesota). Sediments on the United States side of the Detroit River are heavily contaminated with PCBs and other organochlorine compounds, whereas sediments on the Canadian side are less heavily contaminated with PCBs but contain other compounds (OCS, HCB; Thornley and Hamdy (1984), Pugsley et al. (1985)). Sites were situated at a point where the Detroit River becomes separated into two channels by Belle Isle. Traps in Canada were situated at our East Windsor site (Table 1). Traps on the U.S. side of the river were located at Memorial Park, Detroit (42°21'08"N, 82°59'09"W). Direct line distance between the two sites was 3.2 km. Two traps, 40 m apart were operated for 2 h following sunset at each site.

Table 2. Locations of stations sampled at the Niagara and St. Marys rivers, and sunset weather conditions, (NR = Niagara River, SMR = St. Marys River).

Stn.	River	Designation	Latitude (North)	Longitude (West)	Date	Temp. (°C)	Wind$_1$ km h^{-1})
1	NR	Erie Beach	42°53'05"	78°55'47"	5 July	28	calm
2	NR	Ft. Erie Bridge	42°54'42"	78°54'33"	5 July	28	calm
3	NR	Black Creek	42°59'43"	79°01'40"	5 July	28	calm
4	NR	Niagara Gorge	43°07'15"	79°04'25"	6 July	27	calm
5	NR	L. Ontario	43°15'34"	79°04'20"	6 July	27	calm
1	SMR	L. Superior	46°30'51"	84°54'33"	28 June	16	S 30
					30 June	13	W 0-5
					15 August	18	calm
2a	SMR	Bell's Point	46°32'15"	84°13'10"	28 June	16	calm
2b	SMR	Reserve	46°32'02"	84°81'02"	15 August	18	calm
3	SMR	Pine Island	46°19'09"	83°47'25"	29 June	13	W 30
					15 August	18	calm
4	SMR	French Island	46°17'24"	83°47'25"	29 June	13	W 30
					15 August	18	calm

2.2. Sample sorting and contaminant analysis

Samples were weighed and sorted to families of Trichoptera (Hydropsychidae, Leptoceridae, Psychomyiidae) for contaminant analyses by gas chromatography (GC). Other taxa were not used for contaminant analyses. Since the samples collected from the St. Marys River were relatively small, all species of Trichoptera were pooled for analyses. In addition to samples of pooled hydropsychid caddisflies from opposite banks of the Detroit River, two replicate samples of the large hydropsychid, *Macrostemum zebratum* were also analysed from each bank.

One hundred randomly selected caddisflies from each sample were preserved in 70% ethanol and were later identified to genus. All samples (sorted and unsorted) were stored at -20°C until processing or contaminant analysis. Triplicate, or in cases when insufficient material was collected, duplicate samples of adult insects were assayed for 36 OC contaminants (pentachlorobenzene (QCB), hexachlorobenzene (HCB), octachlorostyrene (OCS), 25 PCB congeners, and 8 pesticides). Sizes of samples used for contaminant analysis ranged from 2-5 g (fresh weight), depending on availability. Dry weights of extracted samples were estimated by weighing an additional 2-5 g portion of the fresh or frozen sample, drying at 105°C for 24 h, and reweighing. Dry weights were then calculated by multiplying the fresh weight of the sample to be analysed by the dry weight:fresh weight ratio.

Extractions and contaminant analyses were performed at the Great Lakes Institute analytical laboratory, University of Windsor. Extraction procedure was outlined in detail by Kovats and Ciborowski (1989). Samples were homogenized with mortar and pestle and extracted by solid-liquid column extraction, using a 50% dichloromethane - 50% hexane mixture. Lipids and OC compounds were separated by passage through a Biobeads column. Lipids were weighed following evaporation of solvents from the lipid fraction. Florisil cleanup of the second fraction, using two different solvents, followed by concentration by rotary evaporator yielded two fractions, containing all extracted OC compounds. One µL from each fraction was injected into the GC (Hewlett-Packard, model 5790A) equipped with a fused silica column and an electron capture detector. Specific conditions and methodology used during GC analyses were as outlined by Ciborowski and Corkum (1988).

2.3. Data analysis

Concentrations of individual contaminants in aquatic insect samples were not independent of one another. High correlations were noted among concentrations of all PCB congeners. Accordingly, principal component analysis (PCA) was used to identify groups of associated compounds, using contaminant concentrations in caddisfly adults collected at all sampling stations on the Detroit, St. Clair, Niagara, and St. Marys rivers. Compounds with high variation among replicates (coefficient of variation >50%, n=3) were excluded from the analysis. To simplify presentation of our results, we selected representative compounds (Table 3), based on the PCA. Five PCB congeners (one of each with 4, 5, 6, 7, 8 chlorine atoms per molecule), dieldrin, and OCS were selected. These representative compounds also were used for presenting data on small scale spatial variation in contaminant burden (opposite banks of the Detroit River) and seasonal variation in contaminant burden.

Table 3. Principal component analysis (PCA) eigenvectors for each contaminant showing associations with each of three principal components, and representative compounds selected for visual presentation of contaminant concentrations. Compounds are arranged in decreasing order of their eigenvectors, and values <0.25 have been replaced with zeroes.

Compounds (No. of chlorine atoms)	PC-1	PC-2	PC-3
PCB 141 (6)	**0.928**	0.272	0.000
* PCB 180 (7)	**0.925**	0.302	0.000
* PCB 201 (8)	**0.922**	0.000	0.000
PCB 182 (7)	**0.921**	0.337	0.000
PCB 194 (8)	**0.905**	0.000	0.000
PCB 203 (8)	**0.898**	0.000	0.000
PCB 170 (7)	**0.874**	0.295	0.339
PCB 151 (6)	**0.864**	0.363	0.000
* PCB 138 (6)	**0.853**	0.415	0.000
PCB 153 (6)	**0.844**	0.466	0.000
* PCB 101 (5)	**0.815**	0.375	0.404
DDE	**0.786**	0.349	0.000
* PCB 52 (4)	**0.775**	0.399	0.400
PCB 66 (4)	**0.770**	0.407	0.454
PCB 118 (5)	**0.766**	0.269	0.503
PCB 70 (4)	**0.759**	0.351	0.465
PCB 87 (5)	**0.756**	0.469	0.364
PCB 110 (5)	**0.753**	0.425	0.462
PCB 97 (5)	**0.707**	0.566	0.356
PCB 44 (4)	**0.606**	0.428	0.585
HEPTACHLOR EPOXIDE	0.304	**0.838**	0.000
* DIELORIN	0.353	**0.834**	0.000
-BHC	0.000	**0.775**	0.000
* OCS	0.000	0.000	**0.964**
HCB	0.268	0.386	**0.850**
OCB	0.539	0.000	**0.641**

* Representative compounds

To determine the relationships among contaminant burdens of animals captured from the 4 connecting channels, principal component (PC) scores were used as data for clustering analysis (hierarchical agglomerative clustering, Ward's method (Wishart 1978)) of all samples collected at the Detroit, St. Clair, Niagara, and St. Marys rivers. Since the relative magnitude of PC each score is representative of concentrations of contaminants associated with that component, we plotted mean PC scores of samples comprising each of the clusters. One-way ANOVA followed by Student-Newman-Keuls test (Sokal and Rohlf, 1981) was used to compare mean PC scores of samples falling into different clusters . Contaminant concentrations of insect samples in each cluster were compared to reports of sediment contamination in the literature.

3. RESULTS AND DISCUSSION

3.1. Sample collection

3.1.1. Detroit River

Detroit River traps attracted large numbers of Trichoptera throughout the summer months. The family Hydropsychidae dominated all catches at both sampling stations. Station 1 was situated near marshland, and samples collected at this station were more taxonomically diverse than those from Station 2, often including representatives of aquatic Diptera, Coleoptera, Megaloptera, and terrestrial taxa. The mayfly Hexagenia (Ephemeroptera: Ephemeridae) was caught in large numbers at Station 2 only during its peak emergence period, in late June. No Hexagenia were captured at Station 1.

3.1.2. St. Clair River

Collections at the St. Clair River yielded fewer insects than those from the Detroit River. Hydropsychidae and Leptoceridae dominated St. Clair River samples. Sufficient numbers of Hexagenia for GC analysis were caught in late June.

3.1.3. Niagara River

Niagara River traps quickly attracted enormous numbers of Trichoptera. At several sites, the insects were so abundant that the trap had to be shut off 15 minutes after sunset because the light trap catchment container was completely filled and all collecting jars were exhausted. No Ephemeroptera were encountered.

3.1.4. St. Marys River

Weather was cold and rainy during the June and August collection periods on the St. Marys River. Trichoptera samples collected were small and diverse. A few Hexagenia adults were observed swarming during early evening at Pine Island in June but they were not attracted to the trap. An unusually early emergence of Hexagenia from the St. Marys River (D. Schloesser, Michigan Dept. of Natural Resources, personal communication) coupled with unseasonably cool temperatures during the collection periods may have contributed to the low abundance of these animals at trap sites.

3.2 Contaminant concentrations

3.2.1. St. Clair River

Hydropsychidae collected at St. Clair River stations contained the highest levels of HCB, OCS, and QCB recorded among all connecting channel samples, and elevated levels of PCBs (Fig. 1). Octachlorostyrene and associated compounds are found in high concentrations in St. Clair River sediments along the entire length of the river (Upper Great Lakes Connecting Channels Study (UGLCCS 1988)). Concentrations of PCBs are elevated in bottom sediments along the industrial waterfront, south of Sarnia (corresponding to our Station 4; UGLCCS 1988). Concentrations of PCBs in sediments downstream of this area may also be elevated due to inputs from electrical power generating stations, and/or downstream transport. Pesticide levels were elevated in St. Clair River animals, but no previous reports of sediment pesticide contamination were available for comparison.

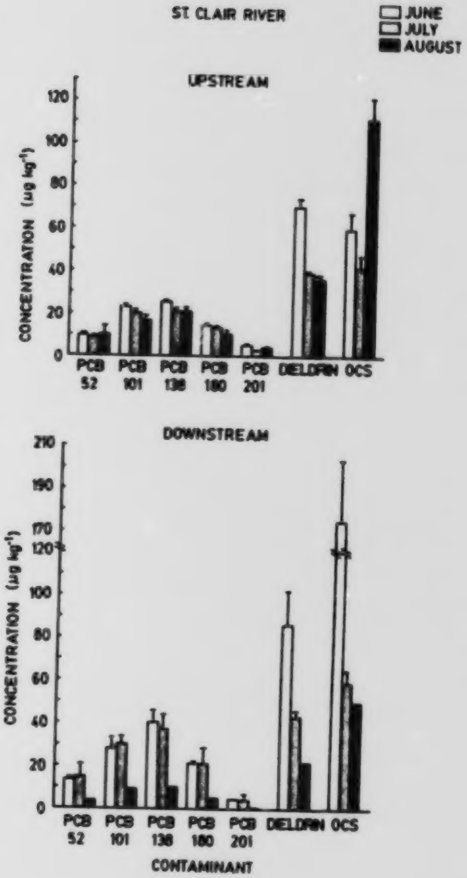

Figure 1. Mean (±1 S.E., n=3) concentrations of representative compounds in Hydropsychidae collected at different times at the St. Clair River. (PCB numbering follows Ballschmiter and Zell (1980)).

Thus, the concentrations measured appear to reflect the degree of local inputs of contaminants. No definite spatial trends in insect OC contaminants could be discerned, based on our data.

3.2.2. Detroit River

Detroit River Hydropsychidae harboured high levels of PCBs, and elevated levels of all other quantified contaminants (Fig. 2). Significant inputs of PCBs to Detroit River sediments have been reported by UGLCCS (1988) and Thornley and Hamdy (1984). Concentrations of PCBs in insects appeared to parallel sediment contamination pattern. The most likely source of elevated pesticide levels in Detroit River caddisflies is agricultural runoff.

Results of contaminant analyses of Hydropsychidae collected simultaneously on opposite banks of the Detroit River are shown in Fig. 3. All quantified PCB congeners were present in significantly higher concentrations in animals from the U.S. side (one-way ANOVA, $p<0.025$). Levels of OCS and associated compounds were greater in animals from the Canadian side than in those from the U.S. side, and pesticide concentrations were equivalent on both sides. Separately analysed samples of *Macrostemum zebratum*, yielded similar results. However, this animal consistently accumulated higher body burdens of OCS and lower burdens of PCBs than did other hydropsychid caddisflies. The filtering net of *Macrostemum* is of smaller mesh size (5x40 um) than those of other hydropsychid caddisflies (50x70 - 130x250 um; Wallace 1975), which may partially account for the observed differences in contaminant uptake.

Our results accurately reflect local differences in Detroit River sediment contamination as measured by previous studies. Thornley and Hamdy (1984), and UGLCCS (1988) reported considerably higher sediment PCB concentrations on the U.S. side of the Detroit River than on the Canadian side. Elevated levels of OCS and associated compounds in Hydropsychidae caught on the Canadian riverbank relative to those from the US bank may be due to the lack of lateral mixing of river water as it travels downstream from the St. Clair River through Lake St. Clair to the Detroit River (Great Lakes Institute 1986). Inputs of these compounds to the St. Clair River are primarily on the Canadian side (UGLCCS 1988).

Significant cross-river differences in insect contaminant burdens imply limited dispersal by adult insects. Results of dispersal studies of adult caddisflies and mayflies confirm these findings. Mean dispersal distances of commonly light trapped species of Trichoptera ranged from 600-700 m (Kovats and Ciborowski 1989).

3.2.3. Niagara river

Samples of Hydropsychidae from the 3 upstream stations contained elevated levels of PCBs and pesticides (Fig. 4). No spatial trend was noted in contaminant burdens in the upper Niagara River. *Ceraclea* (Leptoceridae) adults from stations 4 and 5 (downstream) harboured much lower levels of all pesticides, slightly lower levels of PCBs, and higher concentrations of HCB, OCS, and QCB than Hydropsychidae from stations 1-3. Kauss (1983) reported low (27-48 µg kg^{-1}) total sediment PCB concentrations for the upper Niagara River and the Chippawa Channel, and very high concentrations (up to 2700 µg kg^{-1}) for the lower Niagara River. Differences in feeding behaviour may be responsible for the different contaminant pattern in the caddisflies analysed. Filter-

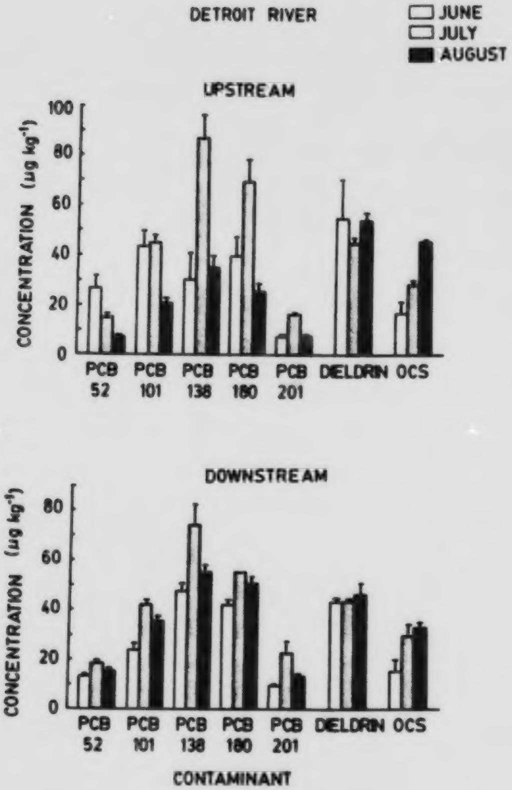

Figure 2. Mean (±1 S.E., n=3) concentrations of representative compounds in Hydropsychidae collected at different times at the Detroit River.

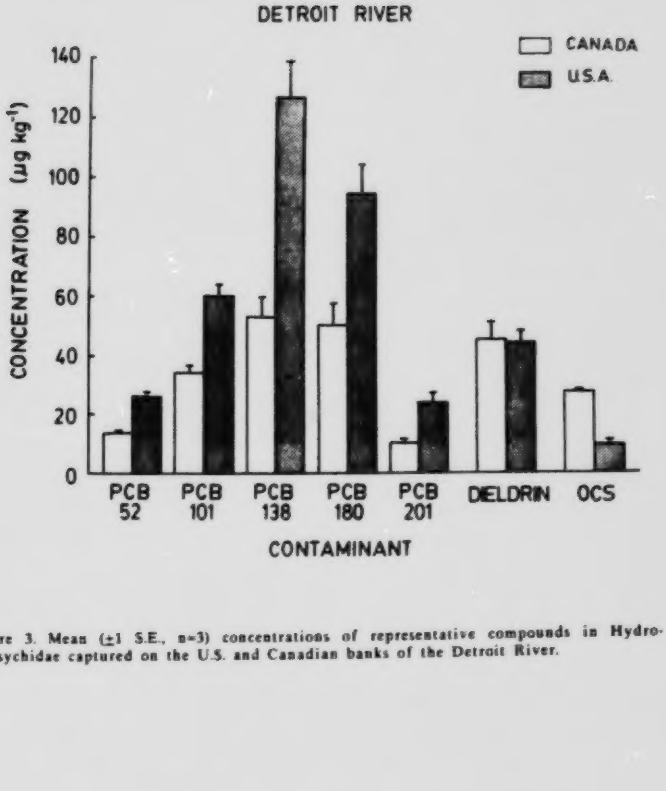

Figure 3. Mean (±1 S.E., n=3) concentrations of representative compounds in Hydropsychidae captured on the U.S. and Canadian banks of the Detroit River.

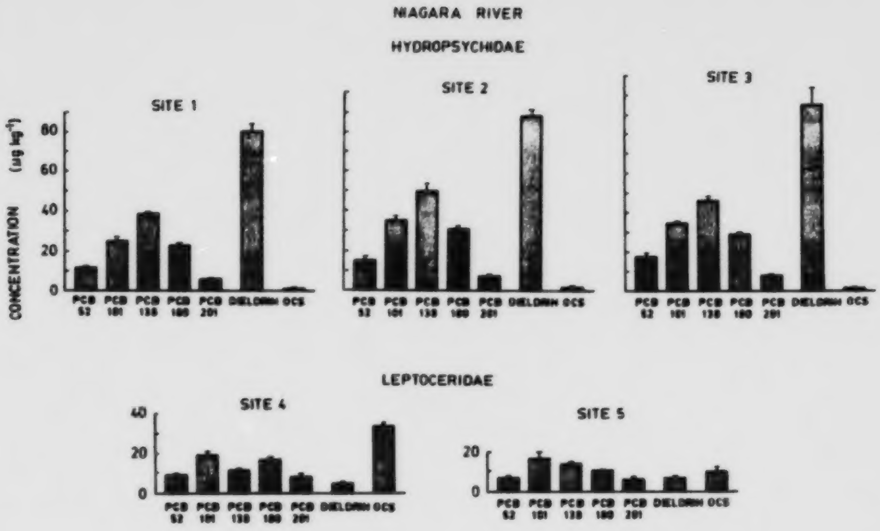

Figure 4. Mean (±1 S.E., n=3) concentrations of representative compounds in Hydropsychidae and Leptoceridae collected at 5 stations along the Niagara River.

feeding, often carnivorous Hydropsychidae may ingest toxic amounts of contaminants through their food, resulting in the eradication of these animals from the lower Niagara River. *Ceraclea*, a grazer and detritus feeder, may survive in such habitats due to lower exposure through feeding. Substrate type is suitable for larvae of hydropsychid caddisflies throughout the length of the Niagara River (Z.E. Kovats, pers. obs.). Lower lipid contents in *Ceraclea* (8.85±0.58% vs. 19.71±0.98% in Niagara River Hydropsychidae) may also contribute to the observed higher contaminant burdens of Hydropsychidae. Detritus-feeding Psychomyiidae, collected at Station 3 (upper Niagara River) carried relatively low body burdens, comparable to those of *Ceraclea* at the downstream stations.

3.2.4. St. Marys River

All samples of Trichoptera (all species pooled) were relatively uncontaminated by OC compounds with the exception of dieldrin, levels of which are also elevated in animals at uncontaminated sites (Kovats and Ciborowski 1989). A slight, nonsignificant downstream increase was noted in contaminant burdens of collected animals (Fig. 5). St. Marys River sediments contain low concentrations of OC contaminants (UGLCCS 1988). Therefore, the degree of OC contamination of our samples of caddisflies was indicative of local sediment contamination.

3.3. Temporal variation in contaminant burden

Contaminant burdens of adult caddisflies collected from the Detroit and St. Clair rivers varied unpredictably with time. PCB concentrations varied little from June to August in St. Clair River Hydropsychidae (Fig. 1), excluding the single replicate of the small August sample from the downstream station, which consisted of mixed Trichoptera. Concentrations of pesticides and PC-2 compounds varied greatly during the same time period. PCB concentrations were greatest in July in Detroit River Hydropsychidae (Fig. 2), whereas levels of all other contaminants remained relatively constant.

In the Detroit and St. Clair rivers, the contaminants exhibiting the greatest seasonal variation were those with the greatest reported inputs. This variation may reflect temporally fluctuating contaminant inputs to river sediments. Although PCBs are no longer produced, industrial waste water and municipal sewer inputs still contribute large amounts of PCBs (approx. 250 kg yr^{-1}) and other organic pollutants to river sediments (UGLCCS 1988). Although data on temporal variation of contaminant inputs into the Detroit River are not available for comparative purposes, our results suggest that monitoring contaminants in adults can reveal relatively short term changes in sediment contamination.

3.4. Similarity of Contaminant Burdens Among Rivers

Reports of sediment contamination revealed that each of the connecting channels contain sediments contaminated by different types and amounts of OC compounds (Kauss 1983, UGLCCS 1988). If aquatic animals accumulate OC contaminants in proportion to sediment levels, there should be close correspondence between types and levels of contaminants in sediments and the animals sampled. Contaminant burdens of similar taxa caught at different stations along a river should be more similar to one another than to burdens of the same taxa from a different river. The dendogram resulting from cluster analysis is shown in Fig. 6. Five distinct groups (clusters) were distinguished by the analysis. Most sampling stations were grouped according to rivers, with the exception of 2 replicate samples of *Macrostemum* and one relatively small sample of Hydropsychidae

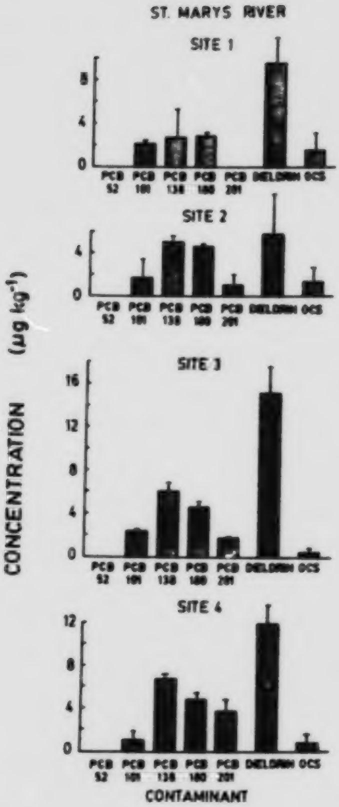

Figure 5. Mean (±1 S.E., n=3) concentrations of representative compounds in Trichoptera (all species pooled) collected at 4 stations along the St. Marys River.

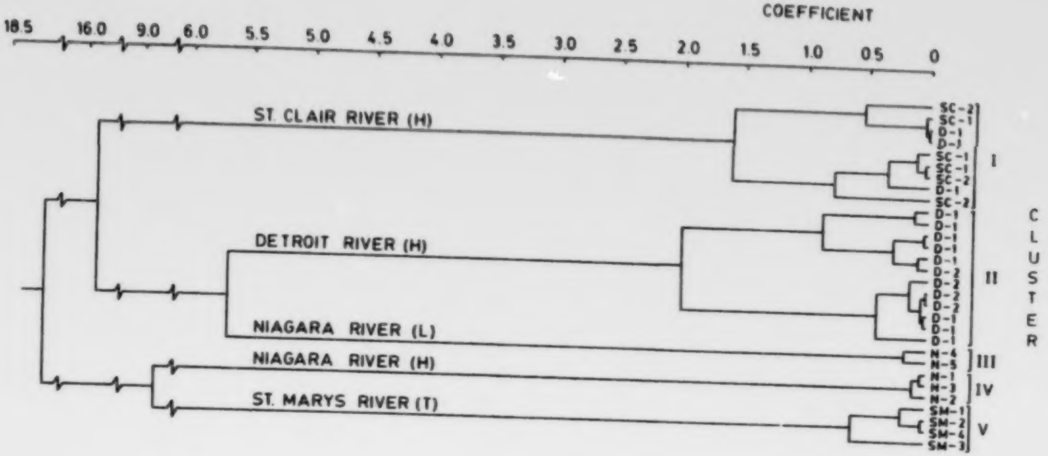

Figure 6. Dendogram of cluster anal,sis of samples collected along the Detroit, St. Clair, Niagara, and St. Marys rivers. Numerals I-V represent groups discussed in text (D: Detroit River, SC: St. Clair River, N: Niagara River, SM: St. Marys River, L: Leptoceridae, H: Hydropsychidae, T: Trichoptera).

(August) from the Detroit River. These samples contained concentrations of PC-3 (OCS, HCB, QCB) compounds more characteristic of St. Clair River samples than of other Detroit River samples.

Cluster I. Samples of Hydropsychidae from the St. Clair and the upper Detroit rivers formed Cluster I. These samples were characterised by relatively low levels of PCBs (PC-1), intermediate levels of pesticides (PC-2), and the highest levels of OCS, HCB, and QCB (PC-3), relative to other connecting channel samples (Figs. 6 and 7). Upper Detroit River samples of *Macrostemum* (replicate samples) were included due to high concentrations of HCB and OCS in those samples. The small August sample of Hydropsychidae was included due to high OCS and relatively low PCB concentrations.

Cluster II. Detroit River samples of Hydropsychidae, with the highest levels of PCBs and intermediate levels of pesticides and PC-3 compounds relative to other contaminants, comprised this group (Figs. 6 and 7).

Cluster III. Leptoceridae from lower Niagara River sampling stations formed Cluster III. These samples contained moderately high concentrations of PCBs, intermediate levels of PC-3 compounds, and the lowest levels of pesticides of the rivers sampled (Figs. 6 and 7).

Cluster IV. Upper Niagara River Hydropsychidae, in Cluster IV, were moderately contaminated by PCBs, had high levels of dieldrin, and relatively low levels of PC-3 compounds relative to the same animals from the other rivers (Figs. 6 and 7).

Cluster V. St. Marys River Trichoptera formed this group, characterized by intermediate levels of pesticides, and lowest levels of all other contaminants compared to samples from other rivers (Figs. 6 and 7). This pattern was also observed in samples of Trichoptera from uncontaminated sites (Kovats and Ciborowski 1989).

Overall, cluster analysis confirmed the occurrence of different and characteristic combinations of OC contaminants in adult Trichoptera emerging from each river sampled. Although differences between concentrations of compounds associated with a given PC were nonsignificant between rivers in some cases (Fig. 7), animals from each river contained a unique combination of contaminants when all 3 PCs were considered. In particular, the caddisfly adults collected from each of the rivers carried body burdens consistent with local sediment contaminant levels.

ACKNOWLEDGEMENTS

We wish to thank Robert Thibert for assistance with collections and sorting. Ms. Sherry Beckett also assisted with field collections. Dr. G.D. Haffner made gas chromatographic facilities available at the Great Lakes Institute (GLI). Dr. L.D. Corkum provided statistical advice and helpful comments on the manuscript. Dr. R. Lazar (GLI) kindly advised us on analytical procedures. This research was funded by the Ontario Ministry of the Environment, Research Advisory Committee. The views and ideas expressed in this paper are those of the authors and do not necessarily reflect the views and policies of the Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

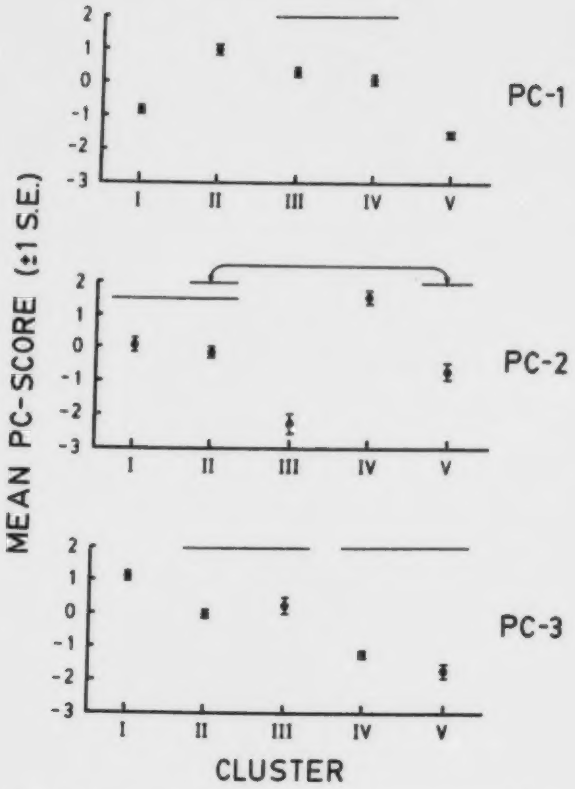

Figure 7. Mean (±1 S.E.) principal component scores of groups distinguished by cluster analysis of samples collected along Great Lakes connecting channels. Means not significantly different from one another are connected by horizontal bars ($p>0.05$, Student-Newman-Keuls test, $n=3$).

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B4

CONTAMINANTS IN ONTARIO SPORT FISH - LONG TERM TRENDS AND FUTURE PROSPECTS.

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Abstract

In 1970, the Province of Ontario began analysing significant numbers of various Ontario sport fish for contaminants of importance or potential importance to human health. The collection and testing of representative samples of the edible portions of many species of fish has been carried out regularly since that time.Data for a variety of contaminants has been used to access long term temporal and spatial trends and the current status of mercury, lead, arsenic, PCB's, mirex, DDT, lindane, chlordane, HCB, OCS, toxaphene and 2,3,7,8 - TCDD (Dioxin) in Ontario fish. The future needs for analysis and criteria development are indicated.

Introduction

As we approach the 1990's, concern for the environment seems to be at an all-time high. Polls tell us that a clean environment is desired by a large majority of the voting public.

There is also the perception that the environment is considerably more polluted than it used to be. The following brief outline will attempt to summarize the status and major trends of contaminants measured in the edible portions of a number of common species of Ontario sport fish. It will also briefly look at the contaminants which will likely be of importance in the next decade.

Mercury

In 1970, anglers in Ontario became aware of the pollution of a number of prime fishing waters with discharges of mercury from chlor-alkali plants in several locations. The fishery of Lake St. Clair was considerably affected by the discharge of mercury from the Dow Chemical Co. near Sarnia. Figure 1a shows the results of annual monitoring for mercury in walleye (Stizostedion vitreum) from Lake St. Clair.

Figure 1b shows a similar, if not so dramatic a decline for walleye from L. St. Francis on the lower St. Lawrence.

The significance of the decline in mean mercury content on the suitability of fish for human consumption can be gauged by Figure 2 which shows the consumption advisory curves for L. St. Clair walleye for five years from 1970 to 1988. In 1970, nearly all sizes of walleye contained over 1.5 ppm mercury and were therefore unsuitable even for very limited consumption. By 1988 nearly all sizes of walleye caught were found to contain less than 0.5 ppm mercury, the limit for commercial sale in Canada.

PCB

Figures 2a, 2b and 2c show the decline in PCB in Coho Salmon (*Oncorhynchus kisutch*) and Rainbow Trout (*Oncorhynchus mykiss*) in Lake Ontario and Coho Salmon from Lake Erie since the 1970s. Current rates of decline are relatively slight. The present PCB level in Lake Erie Coho is about one-third that of the same species in Lake Ontario.

Figures 3a and 3b show the Trends in PCB in Lake Trout (*Salvelinus namaycush*) from Southern Lake Huron and Western Lake Superior.

Figure 3c shows the modeled PCB concentration in Various sizes of Chinook Salmon (*Oncorhynchus tshawytscha*) from six locations; Lakes Ontario, Huron, Michgan and Superior, and from Georgian Bay on Lake Huron and from Green Bay on Lake Michigan. Only the larger sizes of Lake Ontario, Lake Michigan and Green Bay Chinook Salmon exceed the Health & Welfare Canada 2.0 ppm PCB fish consumption criterion.

Figure 4a compares the PCB levels in various sizes of Walleye from the Bay of Quinte on Lake Ontario and from Green Bay on Lake Michgan. Only the larger Walleye from Green bay exceed the [illegible].0 ppm PCB fish consumption criterion.

Mirex

Figures 4b and 4c show the mirex trends for Coho Salmon and Rainbow Trout from Lake Ontario. While there has been little trend in mirex levels in Coho, the Rainbow Trout trend has been a similar decline pattern to those seen for PCB.

Chlordane

Figure 5a shows the decline in Chlordane levels in Lake Ontario Coho Salmon after the removal of this pesticide from the agricultural market in the late 1970s.

DDT

Figure 5b shows the decline of DDT in Lake Simcoe Lake Trout since the cessation in use of this pesticide in the 1960s.

Lead

Figure 5c presents the lead levels for three species of fish from the St. Lawrence river. The source, a company manufacturing tetra-ethyl lead for addition to gasoline, discontinued manufacture in 1985. The reductions in 1984 from the uncontrolled 1983 situation were the result of efforts to control the loss of tetra-ethyl lead to the St. Lawrence river during manufacture. The 1986 levels represent natural background levels of lead in fish flesh.

Discussion

While many contaminants have shown significant declines in the environment, as measured by their concentrations in the edible portions of Ontario sport fish, some locations still contain fish with levels which would indicate the need to control, or improve the control of, sources of PCB and mirex. Other potential contaminants, such as HCB, OCS, the chlorinated phenols and chlorinated benzenes and the PAHs await the development of assessment criteria before their significance in edible portions of Ontario's sport fish can be properly evaluated.

Figure 1a

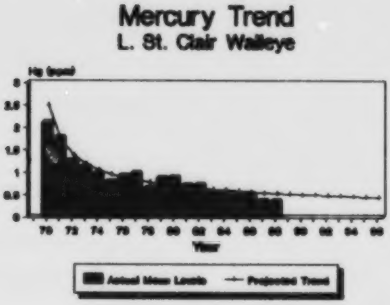


Figure 1b

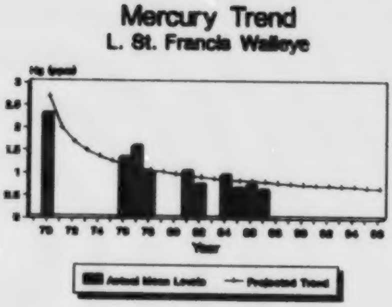
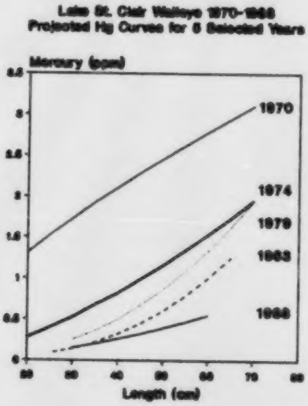


Figure 1c



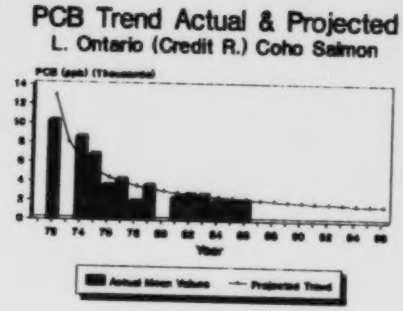


Figure 2a

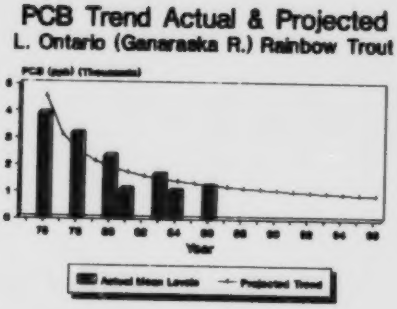


Figure 2b

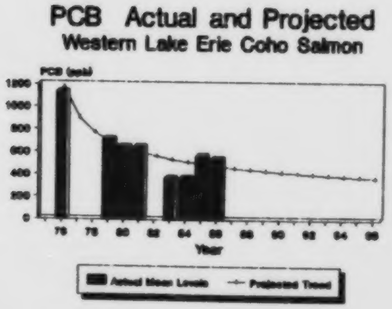


Figure 2c

Figure 3a

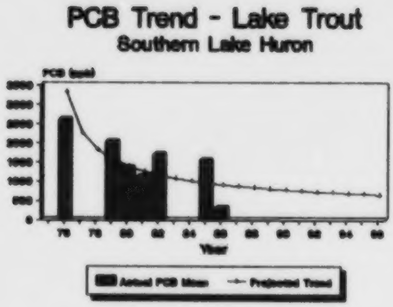
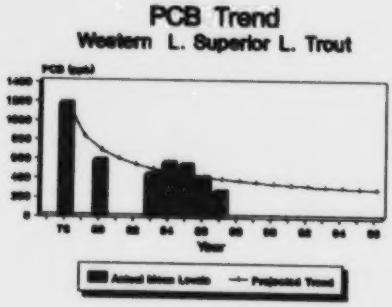


Figure 3b



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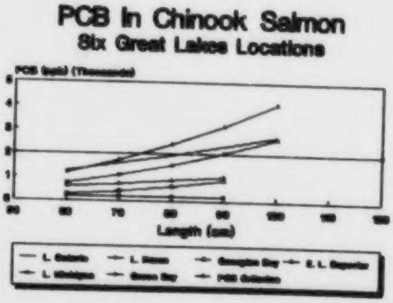
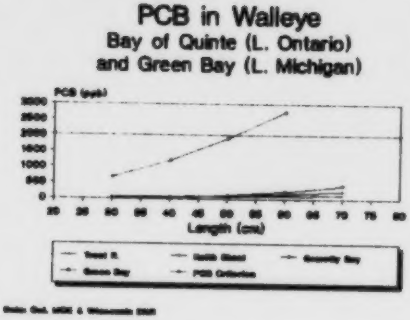
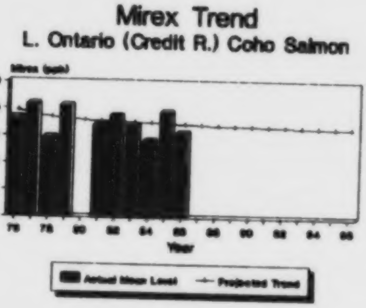


Figure 4a



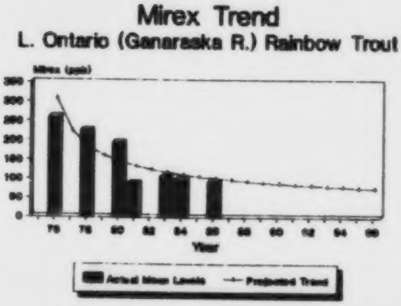
PCB in Walleye
Bay of Quinte (L. Ontario)
and Green Bay (L. Michigan)

Figure 4b



Mirex Trend
L. Ontario (Credit R.) Coho Salmon

Figure 4c



Mirex Trend
L. Ontario (Ganaraska R.) Rainbow Trout

Figure 5a

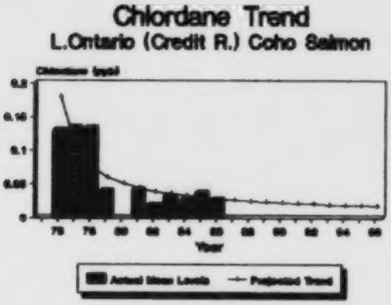


Figure 5b

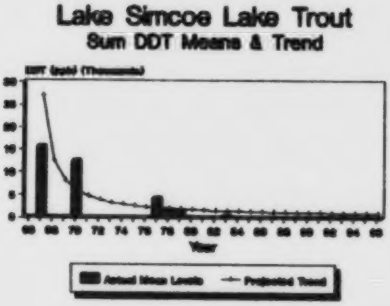
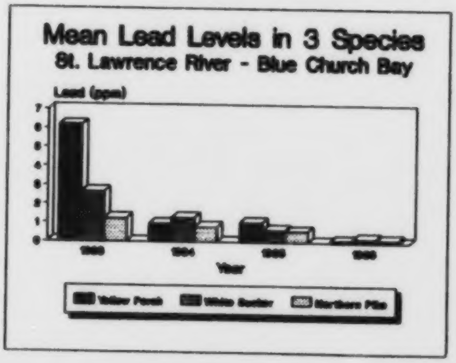


Figure 5c



B5

CONTAMINANTS IN BIOTA AND SEDIMENTS IN SHORELINE HABITATS OF THE BAY OF QUINTE, LAKE ONTARIO.

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ABSTRACT

Levels of Al, As, Cu, Na, Ni and Pb were measured in wetland plants and animals, including *Hydrocharis morsus-ranae*, *Typha latifolia* and *T. latifolia* litter, muskrats, bullfrog tadpoles and the snails *Stagnicola elodes* and *Planorbella trivolvis*. Uptake patterns tended to be specific both for element and organism. Levels of most elements in biota were similar to or below those in sediment, but Cu was bioconcentrated in *S. elodes* (9-83 ppm, $\bar{x}$=41), almost three times higher than in the substrate (6-29 ppm, $\bar{x}$=15) from the same sites. Levels of As, Ni and Pb in muskrat kidneys were below detection limits, but Cu was measurable in all samples (6-18 ppm, $\bar{x}$=9). PCBs in muskrat livers were below 50 ppb in all samples. Sediment fractionation showed that Co, Cu, Ni and Pb were associated mostly with the organic fraction at nearshore sites with intermediate organic content.

INTRODUCTION

Wetlands in the Bay of Quinte, an arm of Lake Ontario, include swamp forests, marshes and beds of floating-leaved and submerged plants. The marshes are areas extending from dry land to an average water depth of one metre, dominated by emergent hydrophytic plants, occupying an area of about 2,800 ha (Crowder and Bristow 1986). The production of fish by lakes in Ontario has been shown to be positively correlated with the area of their surrounding wetlands of all types (Whillans 1989) and the Quinte marshes contribute to the local economy as fish nurseries (c.f. Stephenson 1988). They are also migratory and nesting habitats for waterfowl and habitat for muskrats (Crowder *et al*. 1986). Sports fishing, tourism and to a lesser degree hunting and trapping are regional industries dependent on the wetlands (Michalski 1987).

Eutrophication and contamination have caused declines in habitat quality and populations of waterfowl and muskrats. We have been investigating factors causing such declines, including inorganic and organic contamination. Elements found in sediments at levels most likely to cause toxicity were aluminium, arsenic, copper, chromium, lead, nickel, sodium and zinc (Crowder *et al*. 1988b, 1989, Dushenko *et al*. 1989).

This study focussed on the emergent part of the marshes which, in the Bay of Quinte, usually consist of a dense mat of cattails with a peaty substrate. The organisms selected as being both common and ubiquitous herbivores and detritivores were muskrats, bullfrog tadpoles, two species of snails and two species of plants. We also analysed the litter of the dominant plant, *Typha latifolia*.

Concentrations of PCBs in muskrats, and of Al, As, Cu, Na, Ni and Pb in sediments, plants, litter, snails, tadpoles and muskrats were measured and compared to evaluate concentration and/or magnification in food chains.

Sequential chemical extraction of elements in sediments can provide additional information about their biological availability. To investigate possible bioavailable forms of chromium, cobalt, copper, lead, manganese and nickel, sediments from ten nearshore sites with a range of organic contents were collected, and the element concentrations measured in five operationally-defined fractions.

METHODS

1) Measurement of contaminant concentrations

Collection of samples. Samples of surface sediments, plants, snails and tadpoles were collected from within a 20 ha area at the Pt. Anne marsh complex, east of Belleville on the north shore of the Bay. Surficial substrate, largely matted *Typha* roots with varying amounts of mineral and peat content, was collected from 25 sites, then air-dried and sieved before analysis for elemental concentrations. Organic content was estimated by ignition at 450 °C for 8 h.

Live *Typha latifolia* plants were collected from 24 sites and divided into root and stem portions. *Hydrocharis morsus-ranae* plants were collected at 22 sites and *T. latifolia* litter was collected at 7 sites. Plant samples were rinsed, dried at 90 °C and ground to a fine powder before elemental analysis.

Stagnicola elodes was collected from 25 sites and *Planorbella trivolvis* was collected from 17 sites. For each sample, approximately 35 snails between 10 and 20 mm in shell length were collected and allowed to depurate in clean water, then frozen. Soft tissue was removed from the shells, rinsed and dried at 90 °C before analysis.

Fifteen tadpoles of the bullfrog, *Bufo americanus*, were collected and allowed to depurate in clean water for 48 h, then frozen. They were dried at 90 °C and each individual analysed whole for elemental concentrations.

Carcasses of muskrats, *Ondatra zibethicus*, from 7 traplines around Big Island and Huff Island on the south shore of the Bay were obtained. Kidneys were dried at 70 °C before elemental analysis and livers were used fresh for PCB analysis.

Neutron activation analysis (NAA). Elements including Al, As and Na were measured in sediments, plants and snails by NAA. Technique was similar to that described in Crowder *et al*. (1989).

Atomic absorption spectrophotometry (AAS). All sample types except live *T. latifolia* and *P. trivolvis* samples were analysed for Cu, Ni and Pb using AAS. Tadpoles and muskrat kidneys were also analysed for As by AAS. Sediment and plant material were digested using HNO_3, $HClO_4$ and HF. *Stagnicola elodes* tissue and tadpoles were digested in HNO_3. Muskrat kidneys were digested in HNO_3 and $HClO_4$. All digests were reacidified in 20% HNO_3, and standards were prepared using the same matrix.

Analysis for Cu, Ni and Pb in sediments, plants and muskrat kidneys, and for Cu in *S. elodes* and tadpoles was performed using flame atomic absorption spectrophotometry and analysis for Ni and Pb in *S. elodes* and tadpoles was performed using graphite furnace atomic absorption spectrophotometry. Analysis of As in tadpoles and muskrat kidneys was carried out using a hydride generation method. Certified reference materials used for standardizing analyses were NRCC MESS-1 marine sediment, NRCC SRM-1572 citrus leaves and NRCC TORT-1 invertebrate tissue.

The detection limit for As was 1 ppm for all sample types. For sediment and plant samples, detection limits were 0.05 ppm, 0.6 ppm and 0.6 ppm for Cu, Ni and Pb respectively. For animal samples, detection limits were 0.08 ppm, 0.2 ppm and 0.2 ppm for Cu, Ni and Pb respectively.

Organic analysis. Muskrat livers were analysed for PCBs by gas chromatography using standard techniques. The detection limit was 50 ppb.

2) Element partitioning in nearshore sediments

Surficial sediment cores were collected from ten sites around the Bay of Quinte representing a wide range of different organic contents, measured by loss on ignition at 420 °C for 2 h. Organic content ranged from 0.5 to 65% of sediment dry weight. Sequential extractions were performed by the Queen's University Analytical Services Unit, employing the methods of Tessier *et al*. (1979). Wet sediments were fractionated into five operationally-defined fractions as follows: i) exchangeable ($MgCl_2$, pH7), ii) carbonates (NaOAc/HOAc, pH 5), iii) Fe-Mn oxides (NH_2OH HCl in 25% HOAc, pH 2), iv) organic matter (H_2O_2/HNO_3, pH 2 + NH_4OAc) and v) residual (HF + $HClO_4$). Levels of Co, Cr, Cu, Mn, Ni and Pb were determined in each fraction using flame atomic absorption spectrophotometry. Detection limits were as follows: Co, 0.1 ppm; Cu, 0.3 ppm; Cr, 0.1 ppm; Ni, 1 ppm; Pb, 1 ppm.

3) Bioconcentration of elements in marsh biota

The transfer of contaminants to primary consumers from their medium, or to higher consumers from lower trophic levels can be estimated by calculating concentration factors. The concentration factor (CF) is the ratio of the concentration of a substance in an organism to the concentration in its surrounding medium or in the next lowest trophic level; values greater than 1 indicate bioconcentration (from medium) or biomagnification (between trophic levels) (Campbell *et al*. 1988).

CFs were calculated between plants and sediments, between tadpoles and sediments and between snails and sediments, *T. latifolia* litter and *H. morsus-ranae*. Because of high variances in element concentrations for most groups of samples, two-sample tests were performed to determine whether the means for each group differed. The CF was calculated only where a significant difference existed.

RESULTS AND DISCUSSION

Elemental concentrations in marsh substrate. The average levels of Cu and Ni in the substrate from the Pt. Anne marsh complex (Table 1) fall within the range of concentrations considered to be background for Lake Ontario (Fitchko and Hutchinson 1975, NRCC 1981, Mudroch *et al*. 1988). Aluminum levels are well within normal ranges for soils (Havas and Jaworski 1986). The average level of Pb in the substrates is slightly higher than background levels (Fitchko and Hutchinson 1975, Mudroch *et al*. 1988), and similar to the present average concentration of Lake Ontario surface sediments (Jaworski 1980). Levels of As are higher than the average for Lake Ontario surface sediments given by Traversey *et al*. (1975), and similar to those in other Lake Ontario depositional areas (Mudroch *et al*. 1988). Arsenic is the only element measured that can be considered elevated in these substrates.

Levels of As, Cu, Ni and Pb in the Pt. Anne marsh substrates are lower than in a deep water sediment sample taken from the same part of the Bay in 1979 (Mudroch and Capobianco 1980), while four nearshore sediment samples from the same area had lower mean concentrations of As, Cu and Pb, and higher Na than the Pt. Anne substrates (Dushenko *et al*. 1989). These observations suggest that there is not a simple gradient in sediment element concentrations from deep water to the upper parts of the marshes. The Pt. Anne substrates differ in being more peaty, all having greater than 60% organic content. Accumulation and retention of elements may occur quite differently here than in less organic sediments offshore.

Elemental concentrations in marsh biota. Accumulation of elements in plant and animal tissue was specific for both element and tissue type (Table 1). Aluminum and sodium were accumulated by all biota in which they were measured, whereas As, Cu, Ni and Pb were below detectibility in at least one of the tissue types. Lead, for example, was only detectible in tadpoles, while copper was detectible in everything except tadpoles and *P. trivolvis*.

Copper was accumulated in *H. morsus-ranae*; its average concentration was slightly higher than in aquatic plants from uncontaminated sites on the Moira River (Mudroch and Capobianco 1979). Levels of Al, As, Ni and Pb in *T. latifolia* litter and *H. morsus-ranae* were similar to or lower than levels measured in aquatic plants from uncontaminated areas (Reay 1972 for As, Mayes *et al*. 1977 for Pb, Mudroch and Capobianco 1979 for As, Ni and Pb, NRCC 1981 for Ni, Havas and Jaworski 1986 for Al). Comparisons with other studies must be made cautiously, however, since the levels reported are for different species.

The only element in animal tissue which was elevated relative to background levels was copper. *Stagnicola elodes* had an average concentration of 41 ppm, ranging up to 83 ppm (Table 1). This average is at least twice the level measured in bivalves and crayfish from uncontaminated or slightly contaminated systems (Spear and Pierce 1979). Copper was also measurable in muskrat kidneys, whereas the other trace elements were all below detectibility. Levels of As, Ni and Pb in the other animals were either below detectibility or similar to background or uncontaminated levels (NRCC 1978 for As, Jaworski 1980 for Pb, NRCC 1981 for Ni).

Comparison of concentrations in organisms at the same trophic level revealed species- and tissue-specific accumulation patterns. Litter formed from cattails had higher levels of some elements (eg. Al) and lower levels of other elements (eg. Na) than the live shoots.

Typha latifolia litter and *H. morsus-ranae* also had differing element concentrations (Table 1). These are the two most common plant substrates, and probable food sources, of both species of snail (Greig, unpublished observations). *Hydrocharis morsus-ranae* had significantly higher concentrations of Al, As and Na ($p<0.05$). Levels of Cu and Ni in *H. morsus-ranae* were also higher than in *T. latifolia* litter by more than an order of magnitude, but because of high variances these differences were not significant. Lead concentrations were below detection limits in both tissue types.

Pulmonate snails, such as the two species collected, usually require atmospheric oxygen (Purchon 1977). The snails may have chosen *Typha* litter and *H. morsus-ranae* as preferred substrates because they are the most common floating material in marsh pools and provide easy access to the air as well as for food. Since it was introduced into North America in 1939, *H. morsus-ranae* has rapidly expanded its range and is now very abundant in some marshes in the Bay of Quinte (Crowder *et al*. 1988a). The potential for accumulation, at least of As, Al and Na appears to be significantly higher from *H. morsus-ranae* than from *T. latifolia* litter. If it replaces *T. latifolia* litter as the uppermost floating material in marsh pools, the potential for passage of toxic elements into these snails may be increasing.

Species difference in accumulation also occurred between the two snails. *Stagnicola elodes* had significantly higher levels of Cu, As, Al and Na than *P. trivolvis* ($p<0.05$). Consumption of *S. elodes* by higher consumers therefore poses more of a risk for magnification of those elements than does consumption of *P. trivolvis*.

PCB concentrations in muskrat livers. The level of PCBs in muskrat livers was below the detection limit of 50 ppb in all 63 samples tested.

Element distribution in nearshore sediment fractions. The average distributions of metals amongst different sediment fractions, expressed as percentages, are shown in figure 1. The variance from these means was low in sites with intermediate values (12 to 19 %) of organic matter (LOI). Different fractional distributions were found at the extremes of sediment organic content for all elements except Cu. Cobalt, Cu, Ni and Pb were bound most predominantly to organic matter (> 55 %), whereas Cr was bound in greatest proportion to the residual fraction (71 %) followed by organics (29 %); levels were close to or below detectible limits in other fractions. Large amounts of Co, Cu, Pb and Ni in the organic fraction suggested these metals may be more available to detrital feeders. Manganese distribution was very different with a large percentage bound to exchangeable, carbonate and oxide fractions in addition to the residual and organic phases.

Bioconcentration of elements in marsh biota. The most complete picture of the transfer of elements through the food chain was obtained for *S. elodes* (Table 2). These snails probably feed directly on *H. morsus-ranae*, since they were observed grazing on green plants; snails also feed on detrital material in sediment (Kohn 1983). The CFs between snails and sediment and between snails and *H. morsus-ranae* may therefore represent real instances of biomagnification. The relationship between *S. elodes* and litter, however, is questionable. Although snails were often found on litter, they may have been grazing on epiphytic algae rather than on the litter itself. The only other examples of transfer up the food chain were indicated by a CF of 3.2 for Na levels in *H. morsus-ranae* and sediments, and a CF of 5.0 for Na levels in *P. trivolvis* and litter.

Copper concentrations in muskrat kidneys and local sediments. Copper in muskrat kidneys averaged 8.1 ppm and ranged up to 18 ppm. The concentration in samples from Huff Island traplines and Big Island traplines differed significantly (11.0 ppm vs. 7.6 ppm; $p<0.05$). Nearshore sediments from the two areas also differed, with Huff Island sediments having 25 ppm Cu and Big Island sediments having 8-10 ppm (Dushenko, unpublished data). Only 7 muskrats were taken from Huff Island, however, and sampling bias in the age, sex, weight and diet of the animals could also account for the difference (cf. Erichsen and Lindzey 1983 for Pb).

ACKNOWLEDGEMENTS

We wish to thank Mr. R. Redner, Mr. S. Hamilton, Mrs. K. Vowinkel and members of the Belleville Fish and Game Club for obtaining muskrat carcasses. We also wish to thank Dr. A. Scheuhammer, Mrs. V. Glooschenko and Ms. C. Vardy. This research was funded by the Ontario Ministry of the Environment and the World Wildlife Fund.

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Figure 1. Average distribution of six selected metals , expressed as a percentage of the total, in different sediment fractions of ten nearshore sites.

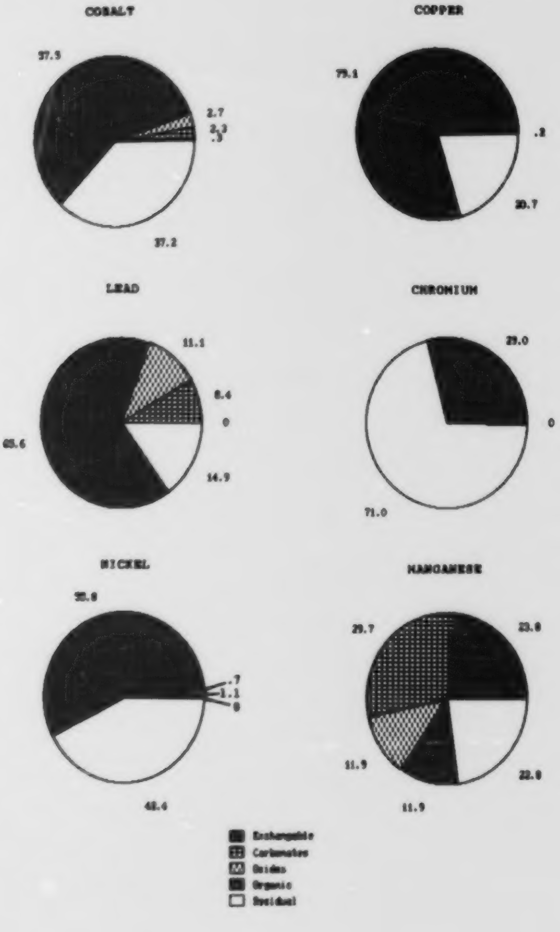
COBALT
57.5
2.7
2.3
.3
37.2
COPPER
79.1
.2
20.7
LEAD
11.1
8.4
0
65.6
14.9
CHROMIUM
29.0
0
71.0
NICKEL
55.8
.7
1.1
0
42.4
MANGANESE
29.7
23.8
11.9
22.8
11.9
Exchangeable
Carbonates
Oxides
Organic
Residual

Table 1. Mean values for selected elements in sediments and biota from marshes in the upper Bay of Quinte, Lake Ontario. All measures are per unit dry weight, ± standard deviation. Numbers in parentheses are ranges. Dashes indicated elements not measured.

Sample Type	Cu(ppm)	Ni(ppm)	Pb(ppm)	As(ppm)	Al(ppm)	Na(%)
Sediment (n=25)	15.4 ±6.3 (4.3 - 28.8)	13.3 ±11.2 (0 - 32.0)	41.0 ±15.2 (15.7 - 65.0)	10.2 ±4.8 (3.8 - 23.9)	14900 ±11900 (3500 - 49900)	0.32 ±0.33 (0.06 - 1.21)
Typha stems (n=24)	--	--	--	b.d.[1]	25 ±25 (15 - 150)	0.26 ±0.09 (0.10 - 0.44)
Typha roots (n=24)	--	--	--	--	1000 ±975 (40 - 2910)	0.28 ±0.10 (0.12 - 0.48)
Typha litter (n=7)	1.8 ±0.7 (1.1 - 3.1)	0.4 ±1.1 (0 - 3)	b.d.	b.d.	130 ±108 (40 - 360)	0.06 ±0.03 (0.04 - 0.12)
Hydrocharis morsus-ranae (n=22)	17.5 ±26.8 (2.9 - 103.0)	12.7 ±33.7 (0 - 151)	b.d.	2.0 ±2.1 (0 - 6.3)	195 ±55 (120 - 280)	1.03 ±0.19 (0.61 - 1.36)
Stagnicola elodes (n=25)	40.7 ±22.0 (9.2 - 82.9)	5.4 ±3.7 (1.9 - 17.0)	b.d.	4.4 ±1.0 (3 - 6.9)	960 ±950 (200 - 4500)	0.66 ±0.08 (0.48 - 0.84)
Planorbella trivolvis (n=17)	b.d.	--	--	2.9 ±0.8 (1.8 - 4.3)	210 ±270 (20 - 890)	0.30 ±0.08 (0.21 - 0.52)
Tadpoles (n=15)	b.d.	12.9 ±5.7 (7.5 - 29.2)	4.4 ±1.7 (1.1 - 7.8)	0.6 ±1.0 (0 - 2.6)	--	--
Muskrat kidneys (n=56)	8.1 ±1.9 (6 - 18)	b.d.	b.d.	b.d.	--	--

[1] below detection limits

Table 2. Concentration factors (CFs) for Al, As, Cu, Mn, Ni and Pb in *Stagnicola elodes* vs. sediments, *Typha latifolia* litter and *Hydrocharis morsus-ranae* plants.

Sample Type	*Al*	*As*	*Cu*	*Mn*	*Ni*	*Pb*
sediment	0.1	0.4	2.6	2.1	0.4	0
Typha litter	7.4	--[1]	22.6	11.0	13.5	0
Hydrocharis	4.9	2.2	2.3	0.6	n.s.d[2]	0

[1] CF not calculable because denominator = 0
[2] means for the two groups of values not significantly different

B6

CARCINOGENICITY TESTING WITH A RAINBOW TROUT BIOASSAY

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ABSTRACT

The rainbow trout microinjection assay is a simple and sensitive bioassay technique with applications to carcinogenicity testing of single chemicals and complex environmental mixtures. The microinjection assay has been used to test recognized chemical carcinogens (aflatoxin B_1, 7,12 dimethylbenzanthracene), and extracts from contaminated sediments. Amounts of chemical used in these assays (ng to μg) are comparable to those used in *in vitro* genotoxicity assays such as the Ames test. Recent modifications to the assay procedure have reduced the latency period for tumor development from 12 mo to 6 mo, and have introduced the potential for testing environmental chemicals for tumor promoting activity. The trout microinjection assay is currently being used to test the carcinogenicity of industrial effluents; specifically, the effluents from kraft pulp mills.

INTRODUCTION

In a recent review, Krayhill et al (1) analyzed the toxicological data for the approximately 1,600 chemicals which have been detected in drinking water supplies. Greater than 95% of these aquatic contaminants have not been adequately tested for carcinogenic or mutagenic activity. This is perhaps not surprising when one considers that there are over 63,000 registered chemicals in common use, and approximately 6,000 new chemicals are registered every week. In the absence of adequate testing programs for individual compounds, it is logical that these chemicals be tested at their source as they are discharged into the environment.

Liquid industrial effluents have been recognized as one of the largest sources of chemical contaminants in the aquatic environment (2). Most primary industries use large amounts of water, either as a solvent or as a coolant. For instance, the pulp and paper industry discharges over 200,000 litres of water per metric ton of product. In Ontario there are over 300 industries which release liquid effluents from approximately 1,000 discharge pipes.

The mutagenic and/or carcinogenic potential of a few industrial effluents have been characterized by chemical analysis and *in vitro* mutagenicity testing of effluent extracts. Douglas et al (3), Holmbom et al (4) Leach (5), and Kringstad et al (6) reported mutagenic activity in chlorination-stage effluents from kraft pulp mills. Pelroy et al (7) and Epler et al (8) found Ames test-positive mutagens in shale-oil fuels, as well as in the effluents from shale-oil refineries. Metcalfe et al (9) reported mutagenic activity in extracts prepared from the suspended particulates of oil refinery effluents. Kirk and Mitchell (10) identified several chlorinated compounds with carcinogenic potential in chlorinated effluents from the food industry.

It is important to note that many of the components of these industrial effluents with carcinogenic potential consist of relatively polar, water-soluble compounds. This suggests that these compounds are not "classical" environmental carcinogens, such as polynuclear aromatic hydrocarbons (PAHs), but are relatively unknown compounds, not normally detected by chemical monitoring programs. However, there are also industrial effluents which do contain high concentrations of classical carcinogens, such as the PAHs in effluents from coking plants and waste-oil refineries (11).

There is indirect evidence that effluent discharges from various industries are carcinogenic. Along coastal areas of Japan, there are large numbers of dermal neoplasms among populations of fish (croaker nibe) living near discharges from pulp and paper mills (12). High numbers of epithelial papillomas were found among black bullheads inhabiting the final oxidation pond of a wastewater treatment facility (13). Several populations of fish inhabiting highly industrialized areas of the Great Lakes have high prevalences of liver tumours (14, 15, 16).

Industrial effluents could be monitored for carcinogenic activity using established *in vivo* carcinogenicity bioassays with rodents. However, these assays are expensive (approximately $750,000 per assay), and time-consuming (1-2 years). Moreover, from a regulatory standpoint, rodent bioassays do not generate ideal data for controlling discharges into the aquatic environment, where populations of aquatic organisms are likely to be affected before human health effects become obvious.

Rainbow trout (*Oncorhynchus mykiss*, formerly *Salmo gairdneri*) are sensitive to a number of chemical hepatocarcinogens, including mycotoxins, nitroso-compounds, and PAHs (18). Liver neoplasms have been induced in trout using several different experimental protocols; including continuous dietary exposure of juvenile fish, and by a single exposure of early life stages to chemical carcinogens. Recently, microinjection of nanogram quantities of carcinogens into eggs or recently hatched fry (sac fry) of rainbow trout has been shown to be a convenient and sensitive assay system for carcinogenicity testing in fish (19, 20). In almost all tests with rainbow trout, chemical carcinogens induce hepatocytic neoplasms, while neoplasms of biliary origin are rare (18).

The main advantage of trout carcinogenicity bioassays is the sensitivity of the test organism. Using the trout embryo microinjection protocol, 100 embryos can be given a carcinogenic dose using the same amount of material (e.g. 10-25 μg) required to give a positive mutagenic response in a single Ames plate. The availability of several different dosing protocols (continuous dietary exposoure, repeated intraperitoneal injections, microinjection of eggs and sac fry) allows the researcher to choose a protocol best suited to the characteristics of the test chemicals.

In this paper, recent modifications to the rainbow trout microinjection carcinogenicity test are described which improve the utility and flexibility of the assay. These modifications include acceleration of the assay by repeated post-initiation exposures to carcinogens, and promotion of the carcinogenic response by repeated post-initiation exposures to carbon tetrachloride (CCl_4). The modifications are currently being incorporated into protocols for carcinogenicity testing of industrial effluents; in particular, the testing of kraft pulp mill effluents for carcinogenic activity.

MATERIALS AND METHODS

Experimental Protocols

The experimental protocols used in this study are summarized in Figure 1. Carcinogenicity assays with the carcinogens, aflatoxin B_1 (AFB1) and 7,12 dimethyl- benzanthracene (DMBA), as well as with sediment extracts, were conducted as single microinjection of rainbow trout at the sac fry stage to carcinogenic solutions. Fish were then raised for periods of 6 mo to 12 mo to necropsy, without additional exposures to carcinogens. Alternatively, trout were microinjected in the sac fry stage with a dose of DMBA, followed by repeated dosing with DMBA at approximately 3 week intervals until necropsy at 6 mo. Finally, in a promotional assay, trout were microinjected with AFB1 in the sac fry stage, followed by repeated dosing with CCl_4 at approximately 3 week intervals, and necropsy at 3 mo or 6 mo post-initiation.

Microinjection Procedure

Rainbow trout of the Kamloops strain were utilized in this experiment. Trout were obtained at the eyed-egg stage of development from a commercial trout farm. Eggs were held in the laboratory until hatched, after which the trout were in the sac fry stage of development and were ready for exposure to carcinogens by the microinjection procedure.

Sac fry were microinjected by the procedure described by Metcalfe et al (20). Briefly, sac fry were anesthetized by immersion in water saturated with carbon dioxide (CO_2). A 0.5 μl volume of AFB1 (13 ng, 25 ng), DMBA (200 ng), or extract from sediment samples (Hamilton Harbour sediment), or DMSO (control) was microinjected into the yolk-sac of each sac fry using a gas chromatography syringe and repeating dispenser.

The microinjected sac fry were placed in tanks supplied with filtered river water. After yolk resorption was completed (trout "swim up"), the fry were fed with a commercial trout diet manufactured by Martin Feed Mills (Elmira, Ontario). The diet contained 40% crude protein, 12% crude fat, 3% crude fibre, 7,500 IU kg^{-1} of vitamin A, 3,000 IU kg^{-1} of vitamin D3, 100 IU kg^{-1} of vitamin E, and 800 mg kg^{-1} ascorbic acid. Fish were raised for up to 6 to 12 mo at water temperatures between 9° and 15°C.

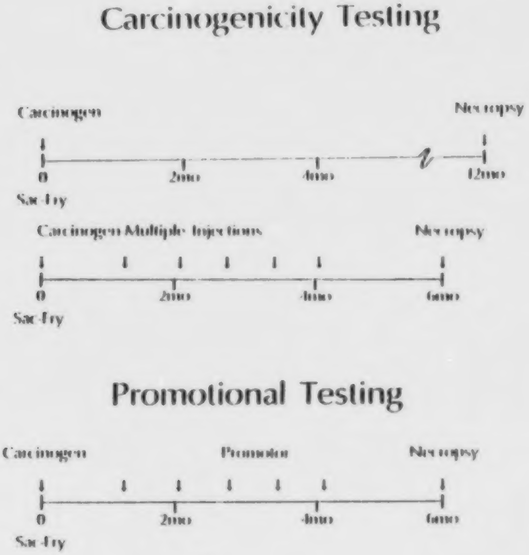
Carcinogenicity Testing
Carcinogen
Necropsy
0
2mo
4mo
12mo
Sac-Fry
Carcinogen Multiple Injections
Necropsy
0
2mo
4mo
6mo
Sac-Fry
Promotional Testing
Carcinogen
Promotor
Necropsy
0
2mo
4mo
6mo
Sac-Fry

Figure 1: A schematic representation of the protocols used in the rainbow trout microinjection assay to test for carcinogenic and promotional activity of chemicals.

Intraperitoneal Injections

Repeated i.p. injections with carcinogens or CCl_4 were done at intervals after tumour initiation in the sac fry stage. Injections were done at a position slightly anterior to the pelvic fins. Fish were i.p. injected every 21 days, for a total of 3, 4, or 7 treatments before necropsy. The first i.p. injection occurred 25 days after initiation. The fish were weighed prior to each treatment, and were injected with a chromatography syringe at doses adjusted for body weight. Different chromatographic syringes were used to inject volumes ranging from 25 µl to 100 µl. Fish were anesthetized using CO_2 saturated water for some early i.p. injections, and for the remaining injections, isoamyl alcohol was used as an anesthetic at concentrations of either 2.86 ml L^{-1} or 3.57 ml L^{-1}, depending on the fish size.

Necropsy and Histopathology

Trout from the various treatments were sacrificed by an overdose of anesthetic (MS-222) and necropsied. Fish were examined externally and internally for grossly visible neoplasms, and the liver was examined and preserved in Bouin's fixative for histological examination. The livers were embedded in paraffin, sectioned at a thickness of 5 µm, and stained with hematoxylin and eosin (H&E). Livers in which lesions had been observed grossly (visual survey) were extensively sectioned for histological confirmation of visual observations. All other livers were surveyed by cutting 5-6 sections from each paraffin block and examining the sections microscopically for evidence of neoplasia (histological survey). The number of neoplasms observed per section were also recorded in the histological survey for analysis of tumor multiplicity. The frequencies of hepatic neoplasms in trout were compared statistically by means of chi-square contingency analysis with a continuity correction (21).

RESULTS

Fish Development and Mortalities

Rainbow trout eggs were received at the eyed egg stage of development, at which time a liver bud, blood circulation, and a beating heart are present (22). Beginning at this stage, the trout are capable of metabolizing indirect-acting carcinogens to reactive intermediates (23). In the sac fry stage, the fish derive their nutritional requirements from the lipid-rich yolk mass for 12-14 days, and during this period carcinogens microinjected into the yolk are presumably absorbed into the fry. At the swim-up stage, the yolk has been consumed and the fry begin to feed voraciously. Water temperatures and feeding regimes were adjusted so that the fish grew quickly. Typically, at 3 mo the mean weight was 8 g, at 6 mo the mean weight was 30 g, and at 12 mo the mean weight was 100 g.

The majority of mortalities were observed during the first 24-48 hours after sac fry microinjection. In the DMSO control group, approximately 10% mortality were observed, while, in treatments with carcinogens and sediment extracts, approximately 20% mortality was observed. Repeated i.p. injections of trout caused approximately 16% mortality per treatment.

Liver Pathology

Liver neoplasms were observed grossly and histologically at necropsies in treatments microinjected with carcinogens or sediment extracts. No lesions were observed grossly in the kidney, spleen, stomach, and gastric caeca. The liver lesions observed grossly at necropsy were round to oval, and their colour was white to pale grey. Their diameter varied from 0.5 mm to 10 mm, and they were located mostly on the dorsal surface of the liver. However, lesions were also observed on the ventral surface.

The histological classification of liver lesions was based upon the criteria outlined by Hendricks et al. (24). Eosinophilic cell foci and vacuolated cell foci were identified in liver tissue, but since it is not clear whether these lesions progress to neoplasms in trout, they were not classified as preneoplastic lesions. Basophilic cell foci were commonly observed, and were classified as preneoplastic lesions. The size of these foci varied from a few cells to 0.5 mm in diameter. Preneoplastic basophilic adenomas were also observed histologically. Their size in liver sections varied from 0.5 mm to 2 mm in diameter. The basophilic adenomas are classified as a preneoplastic lesion, and are distinguished from foci only on the basis of the size (>0.5mm). Cholangiomas were observed in some liver sections. These lesions were composed of ductular elements of biliary origin, and are considered benign bile-duct tumors (24).

Basophilic hepatocellular carcinomas from 0.5mm to 10mm in diameter were noted histologically. For the hepatocarcinogenesis data reported in this paper, only the incidence of hepatocellular carcinomas was included, since these neoplasms are considered true malignancies. In the smaller carcinomas, hepatic sinusoids were distorted in a trabecular pattern, whereas larger carcinomas had a trabecular periphery and a central fibrous stroma. One lesion classified as a poorly differentiated liver hepatocarcinoma (24) was identified, and was characterized by slight eosinophilia, large pleomorphic nuclei, and abundant mitotic figures. Carcinomas of this type are believed to be an advanced stage in the carcinogenic progression, as compared to the trabecular hepatocarcinoma. A single neoplasm was classified as a mixed carcinoma, or hepatocholangiocarcinoma (24). The lesion consisted of neoplastic cells of both hepatocytic and cholangiocytic origin.

Incidence of Hepatic Neoplasms

A) Carcinogenicity of AFB1:

Data on the incidence of neoplasms in rainbow trout following a single microinjection of AFB, are described in detail in Metcalfe et al (20). At the 12 mo necropsy, a dose-response was observed for the two carcinogenesis experiments at AFB1 doses of 13 and 25 ng per embryo. Total incidence of hepatocellular carcinomas, as determined by summing the incidence data for gross and histological observations, was 29% and 11% for the 25 ng and 13 ng treatments, respectively. A previous study on the efficiency of this tumour survey method (9) indicated that the visual survey alone detected 73% of fish with hepatocarcinomas, but the visual plus histologic surveys detected over 90% of fish with hepatocarcinomas.

B) Carcinogenicity of Sediment Extract:

The results of carcinogenicity tests with extracts prepared from sediments collected in Hamilton Harbour are summarized in Figure 2. Trout were exposed to a single microinjection of extract at the sac fry stage and necropsied after 12 mo. Doses are calculated as the equivalent weight weight of sediment (g equivalents) represented by the volume of extract microinjected into each trout embryo. Data are presented on the total number of hepatic neoplasms observed grossly plus the number of hepatic lesions (hepatocarcinomas) observed in the histological survey.

There were hepatic neoplasms observed in trout from all 3 treatments with Hamilton Harbour sediment extract. These lesions were confirmed histologically as hepatocarcinomas. When the results of the visual and histological surveys were combined, the percent positives noted among the Hamilton Harbour treatments showed a 3-point dose response (Figure 2). However, the difference between the percent carcinoma incidence at the two lowest doses was not statistically significant. No hepatic neoplasms were noted in fish treated with an extract prepared from sediments collected at a reference site in Georgian Bay, Ontario (South Bay).

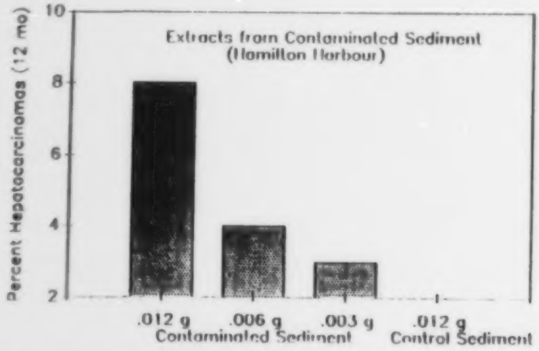

Figure 2: Total hepatic carcinomas in rainbow trout 12 mo after microinjection at the sac fry stage with 3 doses of extract from Hamilton Harbour sediment and 1 dose of extract from sediment from a reference site (South Bay, Ontario).

C) Promotional Assay with AFB1 Initiation and CCl_4 Promotion:

Data in Figure 3 includes the total incidence of grossly-visible and histologically-visible hepatic carcinomas observed after microinjection of sac fry with 20 ng of AFB1 followed by i.p. injections with CCl_4 (1 ml kg^{-1}), or with DMSO (control). At a 3 month necropsy, the AFB1 + CCl_4 treatment showed a higher total incidence of carcinomas compared to the AFB1 group. Figure 4 shows the frequency with which various numbers of carcinomas were observed in each liver from the AFB1 and the AFB1 + CCl_4 groups. Two and three carcinomas per liver were observed more frequently in fish treated with AFB1 + CCl_4. A chi-square test indicated that the AFB_1 multiplicity data followed a Poisson distribution. Thus, in this treatment, the presence of one tumor in the liver section did not enhance the probability of observing other tumours. In contrast, the multiplicity data for the AFB_1 + CCl_4 group followed a negative binomial distribution. In this case, the probability of observing multiple tumours in the liver section was enhanced by the presence of the first.

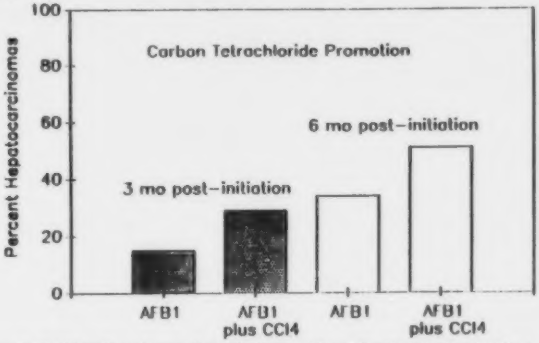

Figure 3: Total hepatic carcinomas observed at 3 mo and 6 mo after microinjection of rainbow trout with AFB1 followed by multiple i.p. injections with DMSO (control) or CCl_4 (promotor).

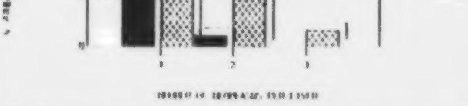

Figure 4: The frequency with which various numbers of hepatic carcinomas were observed in AFB1 and AFB1 + CCl_4 treatments at 3 mo post initiation.

At 6 months, the AFB1 + CCl_4 group showed a significantly higher total incidence of hepatic neoplasms in comparison to the AFB1 group (Figure 3). Multiple tumours per liver were observed frequently in the histological survey at the 6 month necropsy. The AFB1 + CCl_4 group had a greater frequency of multiple tumours than the AFB1 group. However, the mode number was 1 tumour per liver in all treatments. A chi-square test indicated that the multiplicity data observed in the AFB1 and AFB1 + CCl_4 treatments both conformed to a negative binomial distributuion. Therefore, statistically there was no difference in the fit of tumour multiplicity data between initiation alone and initiation with promotion.

D) Single and Repeated Exposures to DMBA:

Histological surveys have not been completed for the incidence of hepatic neoplasms after DMBA exposure, but data on the incidence of grossly-visible lesions indicate that repeated exposure to DMBA significantly increases the incidence of hepatic tumours at a 6 mo necropsy. Single microinjection of sac fry with 200 ng of DMBA produced a very low incidence (1.5%) of hepatic tumours at 6 mo. However, microinjection followed by 7 i.p. injections with DMBA (100 $\mu g\ kg^{-1}$ per injection) enhanced the carcinogenic response to a 5% incidence at 6 mo. Thus, repeated exposures to a carcinogen produced a significant response within a relatively short period (6 mo), in relation to assays conducted with single microinjection exposures (12 mo latency period).

DISCUSSION

In this study, we demonstrated that the rainbow trout microinjection carcinogenesis assay can be modified to accommodate a range of carcinogenicity testing protocols. The test species is sensitive to the carcinogenic effects of AFB1 and contaminated sediment extracts after single exposure to these carcinogens in the sac fry stage. The positive results with sediment extracts, which are described in greater detail by Metcalfe et al (25), represent the first data on the induction of malignant neoplasms in a fish after experimental exposures to a complex environmental mixture. It is anticipated that other environmental mixtures, including carcinogenic industrial effluents, will give a positive response in this assay system. However, when using the single exposure protocols, latency periods for hepatic tumour development are typically in the 12 mo range. The assay would be considerably improved if latency periods could be shortened to 6 mo or less.

Multiple treatments with CCl_4 after initiation with AFB1 promotes hepatocarcinogenesis in fish, and considerably reduces the latency period required to produce a significant carcinogenic response (i.e. 3 months). The criteria used to evaluate the promotional effects of repeated exposure to CCl_4 were based on the relative incidence of preneoplastic and neoplastic lesions in trout liver, and on the number of neoplasms observed per liver section. These data are described in detail in Kotsanis and Metcalfe (26).

Without promotion, a single microinjection of 20 ng of AFB_1 into trout sac fry induced hepatocarcinomas in 12.6% of fish in 3 months and 34.7% of fish in 6 months (total of visual plus histologic survey). When rainbow trout sac fry were injected with AFB_1 at a concentration of 25 ng per sac fry, a total of 29.2% of the trout had hepatocarcinomas at 12 months post-initiation. These data suggest that, in treatments without promotion, the actual incidence of hepatocarcinomas does not change appreciably between 6 and 12 months, although the size of the tumours may increase with time. Hepatocellular carcinomas have been observed after a 10-12 mo latency period in other trout studies utilizing various routes of exposure with several different carcinogens (18). Thus, the appearance of large numbers of hepatocellular carcinomas at 3-6 months post-initiation in treatments with CCl_4 promotion represents a significant shortening of the latency period.

Proliferation of hepatic cells is believed to be an essential part of hepatic carciongenesis, but the actual role of cell proliferation is not clear. Farber and coworkers (27) have suggested that two episodes of cell proliferation are required for hepatic carciongenesis in adult rats: the first one, during exposure to the carcinogen in order to initiate carcinogenesis, and a second one, after exposure to the carcinogen that will promote the initiated cells.

In this study with trout, a first round of hepatic cell proliferation occurs naturally because of the rapid growth of the fry. The second round of proliferation also occurs because of growth of the fish, but it may be enhanced by treatment with CCl_4. In rodents, CCl_4 is known to induce hepatic necrosis, followed by compensatory proliferation of hepatocytes (28). Tumour promotion studies with rats have also shown that CCl_4 is capable of promoting liver cell cancer in rodent species (29, 30). The data from this study show that liver carcinogenesis in fish is governed by universal factors that transcend taxonomic barriers.

The repeated exposure of trout to DMBA significantly enhanced the carcinogenic response at a 6 mo necropsy, in comparison to a single exposure to this carcinogenic PAH. It is possible that repeated post-initiation exposure to DMBA also induces compensatory hepatocyte proliferation by a mechanism analogous to promotion with CCl_4. Alternatively, Farber and coworkers (31) have proposed that liver carcinogenesis in rodents may be enhanced by a process known as the "resistant hepatocyte" model. According to this model, hepatocytes transformed by exposure to carcinogens are more resistant to the hepatotoxic effects of chemicals. Therefore, post-initiation exposures to toxic/carcinogenic chemicals will give a selective advantage to the growth of clones of transformed, resistant hepatic cells. It is possible that this process is taking place in rainbow trout liver as a result of repeated exposures to DMBA following initiation in the sac fry stage.

It is anticipated that the modifications to the rainbow trout carcinogenesis assay described in this study will increase the utility of the assay for the carcinogenicity testing of industrial effluents and other complex environmental mixtures. We now have the capability to conduct bioassays over a relatively short assay period, and there are assay procedures by which chemicals can be tested for tumour promoting activity.

ACKNOWLEDGEMENTS

This work was supported by grants in aid of research from the Ontario Ministry of the Environment and from the Natural Sciences and Engineering Research Council of Canada.
The work was done in collaboration with several researchers; including Vic Cairns and John Fitzsimons of Fisheries and Oceans, Burlington, and Nakos Kotsanis and Gordon Balch within the Watershed Ecosystems Graduate Program at Trent University.

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B7

IMPORTANCE OF GLUTATHIONE S-TRANSFERASE AND CONCURRENT HEPATIC DISEASE IN THE DEVELOPMENT OF LIVER NEOPLASMS IN WHITE SUCKERS (*CATOSTOMUS COMMERSONI*) FROM INDUSTRIALLY POLLUTED REGIONS OF LAKE ONTARIO.

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Abstract

Hepatocellular carcinomas and biliary tract tumors occur more frequently in bottom-dwelling fish such as white suckers (*Catostomus commersoni*) from industrialized areas in Lake Ontario. The metabolism of benzo(a)pyrene, a carcinogenic polycyclic aromatic hydrocarbon (PAH) found in high levels in contaminated sediment, was examined in white suckers from polluted and reference sites in the Great Lakes. HPLC analysis of bile from suckers from western Lake Ontario revealed higher levels of BaP metabolites when compared to suckers from Georgian Bay. Orally administered ^{3}H BaP was excreted in the bile as tritium-labelled conjugates mainly with glutathione, glucuronide and sulfate. The most polar peak co-chromatographed with a double-radiolabelled BaP-glutathione conjugate standard produced in vitro. These findings indicate that glutathione S-transferase (GST)-mediated conjugation is a significant detoxification pathway for PAHs in white suckers. Histopathologic examination of livers revealed a variety of biliary and hepatocellular inflammatory lesions that were often closely associated with hepatic neoplasms. Focal obstruction of bile ducts resulted in preneoplastic proliferations of bile ductules (cholangiofibrosis) and also focal inhibition of GST activity. As hepatic tumors became more malignant, they lost GST protective mechanisms against BaP. Concurrent hepatic disease processes which contribute to loss of GST dependent resistance may be important in facilitating the development of liver neoplasms in fish concurrently exposed to carcinogenic PAHs..

Introduction

White suckers from polluted waterways of the Great Lakes have a higher incidence of liver neoplasms (hepatocellular and biliary) when compared to fish from more pristine locations. These bottom dwelling fish are exposed to carcinogenic chemicals such as polycyclic aromatic hydrocarbons (PAHs) in contaminated sediment. The initiation and progression of neoplasms has been shown to involve a series of genetic perturbations, some of which can be caused by DNA damaging carcinogenic agents (eg. ionizing radiation, reactive electrophiles etc.). Most normal cells have well developed cytoprotective mechanisms (eg. enzymatic detoxification of reactive metabolites, melanin absorption of UV radiation) which normally reduce the occurrence of genetic damage. For example, orally administered PAHs, such as benzo(a)pyrene, are metabolized in the liver of white suckers and subsequently excreted in the bile in the form of water soluble conjugates (Kirby et al., 1989). Alterations in the activity of cellular detoxification enzyme systems involved in resistance to DNA damaging chemicals may render cells more susceptible to the development of cancer. We have recently demonstrated that hepatocellular and biliary carcinomas are deficient in immunoreactive glutathione S-transferase (Hayes et al., 1989). Since GSTs are known to be important catalysts in the detoxification of PAH metabolites in other species we have investigated the role of GST in BaP metabolism in white suckers.

Damage to DNA is normally repaired by various efficient mechanisms in fish and other species (ie. excision repair, alkyltransferases etc.) (Nakatsuru et al., 1987, Miller et al., 1989). However, DNA damage may become "fixed" or permanent should cell division occur before repair (Farber and Sarma, 1987). Various studies have demonstrated that proliferative stimuli are necessary for BaP-induced liver carcinogenesis (Tsuda et al., 1980; Dock et al., 1988). Chronic cell proliferation is therefore conducive to neoplastic development during concurrent exposure to carcinogens. Therefore, we have examined the occurrence of proliferative liver diseases in white suckers from areas of high prevalence of liver neoplasms.

Methods

Male white suckers were captured from Sixteen Mile Creek near Milton, and the Humber River, Lake Ontario (polluted sites) and from Keeler's Creek, near Owen Sound, Lake Huron and Black Bay, Lake Superior (reference sites) during their spring spawning migrations. Fish (Milton and Owen Sound) were orally administered BaP (2 mg/kg, Sigma Chemical Co., St Louis, MO) in a vehicle composed of distilled deionized water, DMSO (10%) and sodium deoxycholate (1%). The BaP preparation contained 50 µCi/mg of ^{3}H-BaP (New England Nuclear, Boston, MA). At 24 hours after administration, fish were killed and samples of bile were taken from the gall bladder and were frozen at -70° C pending further analysis. Bile was also sampled from untreated fish from both reference and polluted sites.

Histopathology

Liver tissue was removed from central lobes or from areas containing visible gross lesions and placed in saline-buffered formalin for fixation. Tissues were processed for paraffin embedding sectioned at 5 µm and stained with hematoxylin and eosin. Sections were also stained by an immunocytochemical procedure for GST proteins using a primary antibody raised in rabbits immunized with affinity purified hepatic GST proteins from white suckers (Hayes *et al.*, 1989).

Purification of GST

Samples of liver taken from fish from the polluted site were immediately dissected and homogenized in 0.25 M cold sucrose (containing 5 mM HEPES, pH 7.0). Cytosol was prepared as the final supernatant of centrifugation at 10,000g (30 min, 4^{o}C) and 100,000 g (60 min 4^{o}C). Samples of whole cytosol were subjected to SDS-PAGE under reducing conditions. Normal hepatic GSTs were purified by stepwise NaCl (2mM) and S-hexylglutathione (5mM) elution of normal hepatic cytosol from S-hexylglutathione-Sepharose (Sigma Chemical Co., St. Louis, MO) as previously described (Rushmore *et al* ., 1987, Rushmore *et al* ., 1988). GST activity was determined with CDNB as substrate (pH 7.0, 30^{o}C) by the method of Habig *et al* ., (1974). Protein concentrations in cytosol were determined by the Lowry method.

Chromatographic analyses of bile

Samples of bile (20 µl) were analyzed by reverse-phase HPLC by a stepwise water/methanol gradient on a C18 column (Biorad Hipore RP-318; 250 x 4.6 mm) and a Biorad 402 gradient module. The mobile phase conditions consisted of stepwise increases of methanol: 0-30% in 2 min, 30% for 15 min, 30-70% in 3 min, 70% for 10 min , 70-100% in 3 min, 100% for 17 min, 100-0% in 5 min and 0% for 5 min at a flow rate of 1.0 ml/minute. The presence of peaks with 430nm absorbance was monitored with a UV/VIS monitor and fluorescence in the eluate was monitored in a Shimadzu RF 5000 spectrofluorophotometer (Shimadzu Corporation, Tokyo, Japan; excitation 380nm ; emission 430nm) equipped with a 12 µl flow-through cell. The distribution of ^{3}H radioactivity tracer in fractions was determined by LSC. The major conjugate peaks of interest were identified with BaP-3-sulfate and 1-benzo(a)pyrenyl 1-beta-d-glucopyranosiduronic acid standards from the NCI Chemical Carcinogen Repository, Kansas City, MO.

In vitro synthesis of ^{3}H-BaP-^{35}S-GSH standard

BaP-GSH conjugates were generated *in vitro* in a reaction mixture containing 80 µMBaP, 5 mM GSH, 500 mCi/mmol ^{3}H-BaP, 0.15 mCi/mmol ^{35}S-GSH, 50 mg sucker liver microsomes and 4 units purified sucker GST brought to a total of 5 ml with 0.1 M KPO_4 sucrose buffer containing 2 mM NADPH. To inhibit epoxide hydrolase activity and maximize the production of glutathione conjugates, 1 mM 1,1,1-trichloro-2-propeneoxide (TCPO) was included in the incubation mixture containing purified GST. Assays were incubated in the dark for 8 hrs at 25^{o}C. BaP metabolites were extracted from the incubation mixture twice with 2.5 ml of chloroform/isoamyl alcohol (10:2).

The aqueous supernatants were added to a 200x12 mm column packed with XAD2 resin (Mandell Scientific, Guelph, Ontario) and free GSH was removed by elution with 100 ml of distilled water (Hernandez *et al.*, 1980). BaP-GSH conjugates were then eluted from the column with methanol (100 ml), lyophylized and reconstituted in 200 μl of distilled water prior to HPLC analysis. HPLC analysis was performed as previously described in Materials and Methods. Fractions were collected at 30 second intervals and radioactivity was determinated with a Tracor Analytic, Delta 300 two-channel liquid scintillation system and counting rates were corrected for background and for spill-over of the ^{35}S into the ^{3}H. Counting efficiency was 76% for ^{35}S and 32% for ^{3}H.

Results

HPLC analysis of biliary metabolites

HPLC chromatograms of bile taken from untreated individual fish from Sixteen Mile Creek, Oakville, Ontario (polluted site) and from a reference site (Black Bay on the north shore of Lake Superior) revealed a complex profile of moderately and highly polar peaks that had characteristic fluorescent properties for BaP and its derivatives (Fig 1). Chromatograms of Oakville fish had larger, more numerous peaks especially in the highly polar range. HPLC analyses of whole unextracted bile from fish from both collection sites that were treated with ^{3}H-BaP revealed a similar complex distribution of concurrently fluorescent and ^{3}H-labelled peaks of BaP metabolites (Fig. 2). No parent (non polar) BaP was detectable in these bile samples.

Identification of ^{3}H-labelled fluorescent peaks of BaP metabolites produced *in vitro* by comparison to BaP metabolite standards revealed that two of the water soluble BaP metabolites coelute with the glucuronide and sulfate conjugates of BaP (Fig. 3). Treatment of bile samples with β-glucuronidase (500 U) resulted in a reduction of the glucuronide peak. A more polar maj peak was subsequently identified as a BaP-glutathione conjugate by its coelution with a double radiolabelled standard (^{3}H-BaP-^{35}S-GSH) produced *in vitro* (Fig. 4). Inhibition of epoxide hydrolase activity *in vitro* resulted in a reduction of all water soluble metabolite peaks except this glutathione conjugate.

Gross pathology

The liver of white suckers is diffusely distributed between loops of intestine, stomach and spleen. Long thin lobes of liver often extended caudally towards the anus. Architecturally, the liver of white suckers (and other teleosts) are arranged in tubular units (in contrast to the acinar pattern of mammalian liver) consisting of several layers of hepatocytes arranged radially around central sinusoids. Bile ducts are not arranged in triads but are scattered throughout the parenchyma as are melanomacrophage centers and exocrine pancreatic acini. There are varying degrees of cytoplasmic vacuolation depending on sex and spawning or nutritional status.

The caudal liver lobes were frequently dark green and atrophic due to segmental bile duct obstruction and hepatocellular atrophy. Neoplasms were visible at necropsy as pale brown, firm, raised, well circumscribed masses approximately 15-20 mm in diameter. Smaller dark brown foci were visible on the surface of the liver of some fish.

Histopathology

Foci of hepatocellular alteration were arranged in well delineated densely populated basophilic nodules of hyperplastic hepatocytes frequently surrounded by melanomacrophage centers and often in close association with areas of cholangiofibrosis. Occasionally, distinct foci were present within larger altered nodules. Hepatomas and hepatocellular carcinomas were characterized by expansive growth, cellular atypia and anaplasia.

Cholangitis was evident surrounding tortuous bile ducts with focally necrotic and hyperplastic epithelium with associated leukocytic infiltrates. In many livers, focal areas of proliferating bile ductules (cholangiofibrosis) were also observed. These were distinguishable from focal nodular expansive bile duct adenomas and carcinomas. The distribution of cholangiofibrosis was segmental and predominantly at peripheral sites in the pendulous lobes that were subject to segmental bile duct obstruction. Trematodes were occasionally observed in association with inflamed fibrotic bile ducts. Diffuse zones of hepatocellular necrosis and regeneration were occasionally associated with migrating ascarid larvae.

GST measurements in fish livers

GST activities in segmentally obstructed were reduced in comparison with the unobstructed adjacent liver. The majority of advanced bile duct and hepatocellular neoplasms were also deficient in immunoreactive GST.

Discussion

These results indicate that white suckers are exposed to PAHs to a greater degree in contaminated areas than in pristine locations and are capable of rapidly excreting BaP as water soluble metabolites in the bile. BaP epoxides are removed either by conjugation to glutathione, or by hydrolysis (epoxide hydrolase) and subsequent glucuronidation of epoxides, which represent significant metabolic pathways in these fish. Studies have shown that microsomally activated BaP can form DNA adducts in several species of fish (Varanasi et al., 1986; Nishimoto and Varanasi, 1985). Also, GST-mediated conjugation has been shown to inhibit the binding of BaP reactive epoxide intermediates to DNA (Hesse et al., 1980; Hesse et al., 1982; Jernstrom et al., 1985). Therefore, it is reasonable to hypothesize that the loss of GST activity would render hepatocytes more susceptible to genetic damage and related consequences.

We have recently demonstrated that advanced liver neoplasms in white suckers are deficient in immunoreactive GST (Hayes et al., 1989). This would suggest that the loss of GST is important in the progression of liver tumors in these fish. In addition to catalyzing the conjugation of reactive epoxides, GSTs also bind to a broad range of nonsubstrate ligands (Ketterer et al., 1988). It has recently been shown that glutathione S-transferase activity is inhibited by elevated intracellular concentrations of bile acids (Boyer and Vessey, 1987; Boyer et al., 1984; Vessey and Zakim, 1981). Our preliminary work in suckers has shown that hepatic cytosolic GST activity is lower in areas of segmental biliary obstruction. It is reasonable to suggest, therefore, that the cholestatic liver in white suckers is more susceptible to toxic injury by chemicals normally detoxified by GST.

The close association of malignant bile duct and hepatocellular tumors with cholangiolar and hepatocellular proliferation resulting from chronic inflammatory liver diseases may be important in tumor progression in white suckers. Any type of chronic cell proliferation is conducive to neoplastic development, especially if there is concurrent exposure to carcinogens (Solt et al., 1980). For example, activation of chemical carcinogens and the development of liver neoplasms are enhanced by concurrent hepatitis B virus infection in humans and other species (De Flora et al., 1989). Similarly, parasitic infestations can enhance the hepatotoxicity of carcinogens such as aflatoxin (Osuna et al., 1977). Furthermore, studies in rats have shown that the liver is not very susceptible to the carcinogenic effects of BaP unless it is concurrently stimulated to proliferate (by post necrotic regeneration) before DNA repair has occurred (Tsuda et al., 1980; Dock et al., 1988). Thus the occurrence of multiple chronic disease conditions in white suckers likely provide biological conditions in which environmental contaminants such as PAHs are more likely to have a DNA damaging carcinogenic effect. This hypothesized multifactorial pathogenesis of pollution-associated neoplasms in white suckers perhaps explains why some species of fish do not develop liver tumors when exposed to a polluted environment.

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Figure 1

CHROMATOGRAPHIC PROFILES OF UNEXTRACTED BILE SAMPLES FROM WHITE SUCKERS FROM POLLUTED AND REFERENCE SITES.

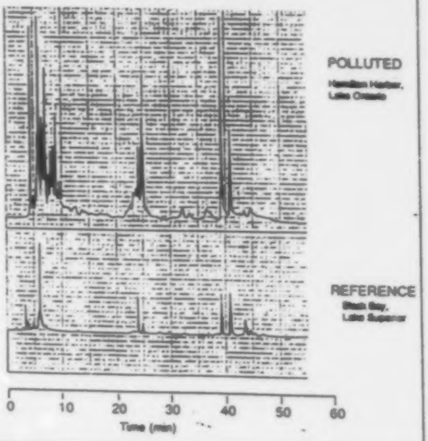


Figure 2

HPLC AND RADIOCHROMATOGRAMS OF WHOLE BILE FROM A WHITE SUCKER TREATED WITH ^{3}H-BAP

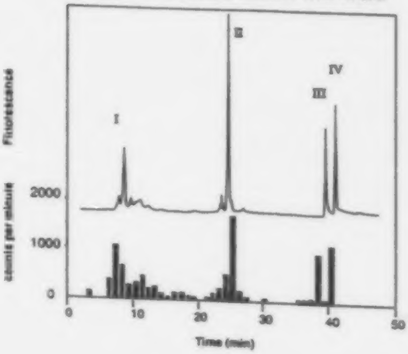
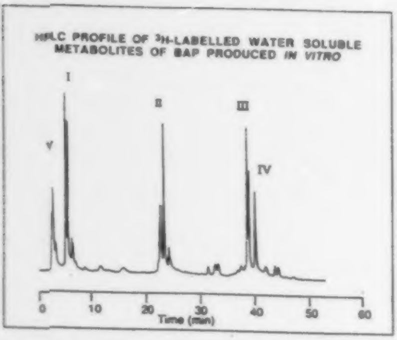


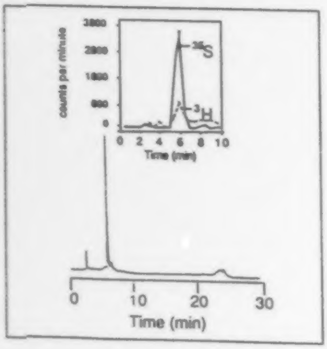
Figure 3



Identity of peaks are as follows: glutathione conjugate (I), glucuronide (II) and unspecified metabolites (III, IV, and V).

Figure 4

HPLC IDENTIFICATION OF A DOUBLE-RADIOLABELLED BAP-GSH CONJUGATE PRODUCED *IN VITRO*



B8

USE OF SPHAERIIDAE CLAMS FOR ASSESSING THE TOXICITY OF CONTAMINATED SEDIMENTS

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INTRODUCTION

A variety of organisms, especially the invertebrates Daphnia spp. (Leonhard 1979a; Buikema et al 1980), Hyalella azteca (de March 1979; Stephenson & Mackie 1986a; Mackie 1988), Orconectes sp. (Leonhard 1979b; France 1986), Chironomus spp. (Anderson 1980), Hexagenia spp. (Fremling & Mauck 1980), Helisoma spp. (Flannagan & Cobb 1979), Amnicola limosa (Servos & Mackie 1986), Musculium spp. (Paparo & Sparks 1976; Mackie 1988), Pisidium spp. (Mackie 1988) and Sphaerium spp. (Stephenson & Mackie 1986b; Mackie 1988) and fish (see Scherer 1979 for use of Pimephales spp., Salvelinus and Salmo spp. and Brachydanio sp.) have been used to test the acute toxicity of organic and inorganic contaminants in effluents. However, the criteria for selecting bioassay organisms for testing the acute and chronic toxicity of contaminated sediments are different from those for testing effluents. For contaminated sediments, the test organism should: (1) be truly infaunal in habit; (2) exhibit omnipresence of all life stages, with no ecdysal or emergence phases; (3) be sedentary and unable to avoid local sediment conditions by swimming away, like fish; (4) be ovoviviparous so that the effects of contaminants on larval stages, relative to adults, in chronic studies are easily ascertained; (5) be locally abundant; (6) be easily sampled and hardy enough to survive laboratory maintenance; (7) be easily reared and cultured in the laboratory for chronic tests; (8) accumulate and tolerate the levels of a pollutant in the environment; (9) be large enough to provide adequate tissue sample; and (10) exhibit the same correlation between their pollutant content and the average pollutant concentration in the surrounding sediment.

The Sphaeriidae clams are well known to satisfy the first six (1 to 6, above) criteria (see Mackie 1978a, b; Mackie & Qadri 1978; Mackie 1988). However, the suitability of Sphaeriidae clams with respect to the last four criteria (7 to 10) have not been previously addressed. The objectives of this study were to determine if species of Sphaerium, Musculium or Pisidium satisfied criteria 7 to 10, above, for assessing the acute and chronic toxicity of sediments contaminated with cadmium.

MATERIALS AND METHODS

The sphaeriids selected for study were those with cosmopolitan distributions and are locally abundant: Pisidium casertanum, Musculium securis, and Sphaerium occidentale. Sphaerium rhomboideum does not have a cosmopolitan distribution but it is locally abundant and was also used in some studies, as described below. All studies were done between May 15, 1987 and April 15, 1988.

To determine if sphaeriids could be easily reared and cultured in the laboratory, newborn of P. casertanum, M. securis, S. rhomboideum and S. occidentale were obtained from local pond populations and reared in the laboratory and growth rates of each were compared to those in the natural habitat. The populations of P. casertanum, M. securis and S. occidentale are located in two adjacent ponds on the south side of Clair Road, about 100 m east of Brock Road south of Guelph, Ontario. The population of S. rhomboideum is located on the north side of Puslinch Road 15 at the junction of Victoria Road south of Guelph. The culture dishes consisted of 100 mm dia X 50 mm high Pyrex dishes containing different substrate and food materials (Table 1). A nylon mesh (1-mm openings) basket whose outside diameter was slightly smaller than the inside diameter of the culture dish was inserted into the culture dishes before adding any materials. This enabled relatively easy removal of all clams for determinations of survival and growth. 5 to 10 specimens, usually newborn, were put into each growth dish and each treatment was replicated 3 times.

The growth rates of species reared in the laboratory were determined from average shell lengths of the 10 specimens taken at two-week intervals in each growth dish. The growth rates of species in their natural habitats were determined from length-frequency analysis of approximately 100 specimens collected at approximately two-week intervals during the summer months (May to October). Clams were measured with an ocular micrometer fitted to a Wild M5 microscope.

In order to determine if sphaeriids: (a) could accumulate and tolerate levels of pollutants in the environment; (b) are large enough to provide adequate tissue sample, and (c) exhibit the same correlation between their pollutant content and the environment (see criteria 8 to 10 above), *S. rhomboideum* was maintained for 15 days in water and sediments spiked with cadmium. This species represents a typical large species of sphaeriid, but specimens were selected to represent the smallest and largest likely to be analyzed for tissue levels of pollutants. Water, sediment and clams of both *P. casertanum* and *S. rhomboideum* from each habitat were analyzed for natural background levels of cadmium.

A range of small (4 mm shell length) to large (1 cm shell length) specimens of *S. rhomboideum* were maintained for 15 days in 14-cm wide X 22-cm long X 9-cm high Tupperware plastic containers with a combination of either pure quartz sand, 1:1 mix of quartz sand and pond sediment, cadmium-spiked quartz sand or pond sediment and either 10% well water or 10% well water spiked with cadmium. All containers were acid washed in 5% HNO_3 before use. In order to determine the source (i.e. sediments or water) of cadmium taken up by the clams, 5 clams were suspended 1.5 cm above the sediments using a plexiglass rack with 1-mm (opening size) nylon mesh bottom. Sediments and water were added to the dishes 1 day prior to adding clams.

The pond sediment was spiked with cadmium by adding 750 ml dry pond sediment < 2 mm dia to 1 L of deionized-distilled water containing 0.1 mg Cd. The water was decanted off after 2 days and then quartz sand was added in equal volume to the pond sediment and thoroughly mixed.

Cadmium-spiked quartz sand was prepared by adding 2 L of quartz sand to 2 L of deionized-distilled water containing 0.1 mg Cd L^{-1}. After 2 days the water was decanted off and the sand was measured in the wet state.

The levels of cadmium used in the chronic toxicity studies were determined from a 96-h static bioassay to determine first the acute toxicity level of cadmium in quartz sand and then the safe level by multiplying the LC50 value by 1/2000, as recommended by Abbasi & Soni (1986). Quartz sand was mixed with deionized-distilled water containing 0, 0.5, 1.0, 2.0, 4.0, 6.0 and [illegible] mg Cd L^{-1} at pH 5.0. Each concentration was replicated three times and ten specimens of *P. casertanum* were placed on the sediments and ten on a plexiglass rack with 1-mm mesh to suspend the clams in the water column above the sediments in each culture dish. Death of the clams was determined by cessation of the heartbeat visible through the semi-transparent shell of the pill clams. Previous studies (unpublished data) showed that cessation of the heartbeat is a more sensitive indicator of death than a gaping shell, which is usually used to determine death in bivalves. However, the heartbeat is not easily visible in some species of bivalves.

10% well water was used throughout the experiments, including growth. The well water was obtained from the University of Guelph wells and had an average total hardness of 300 mg $CaCO_3$ L^{-1}. $CdCl_2$ was used to prepare stock solutions of 0.1 mg Cd L^{-1} using 10% well water.

Cadmium levels in water, sediment and clams were measured by tungsten furnace atomic absorption spectrophotometry (Scintrex AAZ-2 with Zeeman background correction). Clams were wet-ashed in 1.5-mL micro-centrifuge tubes following the methods of Stephenson & Mackie (1988a), but using 2X the volumes for *Sphaerium rhomboideum*. Both shell and tissue were digested and analyzed in newborn clams, but only the tissue was digested and analyzed for all other length classes. It was not necessary to pool samples (specimens) of clams in any digestions since cadmium was detectable in all specimens. Any dilutions necessary were made with 5% HNO_3. 500 mg samples of sediments were digested in 13 mm dia x 100 mm long glass tubes with loose-fitting plastic caps and analyzed following the techniques of Stephenson & Mackie (1988b). 10-mL water samples, with 1 mL of 5% HNO_3 from each treatment were analyzed for cadmium content after storing at 4 C for 1 to 2 wks. All measurements on the Scintrex were replicated at least 3 times.

RESULTS AND DISCUSSION

Survival, Growth and Reproduction

Survival of all four species on artificial substrates and food was poor to excellent, ranging from 0 to 100% (Table 1). On quartz sand alone, good growth was achieved only on a diet of *Chlorella emersonii* for most species (Table 1). In general, without willow leaves large proportions of natural sediments tended to reduce survival and growth. Apparently the organic material imposed a high BOD which depleted the oxygen supply in the culture dishes. Hence, dishes that contained algae had good survival, suggesting that the algae replenished the dissolved oxygen supply. However, since growth of clams in many culture dishes that contained algae was rather poor to negligible, it is doubtful that the algae was a good source of food for the clams.

Reproduction of all sphaeriids was significantly reduced in the growth experiments relative to that seen in the natural habitats (Table 2). In general, reproduction in the laboratory cultures approximated that in the natural habitat only when natural conditions were provided. This observation was also made by Mackie & Qadri (1978) and Mackie & Flippance (1983). Mackie & Flippance (1983) also found that leaves were important for a source of calcium and some food for *M. securis* and without leaves growth and reproduction of the clams was significantly reduced without leaves. However, in studies examining the chronic toxicity of inorganic contaminants in sediments, it is adviseable to eliminate organic materials or at least keep the amounts in the artificial sediments to a minimum since they tend to bind most metals.

Hence, the most significant results in this study are those on 100% quartz sand. Unfortunately, significant amounts of growth and reproduction on quartz sand alone is difficult to achieve. Only when the algae, *C. emersonii*, was provided was any appreciable growth obtained. However, in most cases growth was negligible and reproduction was significantly lower than those seen in the natural habitat. In conclusion, the use of fingernail clams in chronic toxicity studies involving purely inorganic sediments as a maintenance medium will yield results that do not reflect 100% growth and reproduction relative to natural populations. Since none of the sphaeriids tested could be easily reared and cultured in inorganic sediments for chronic toxicity tests, they are not a viable test organism in sublethal bioassays of contaminated sediments.

The use of Sphaeriidae in lethal toxicity studies of contaminated sediments, however, is promising. In the range finding tests to determine the levels of cadmium to use in the chronic toxicity studies, the 96hr LC50 values obtained (Table 3) are very similar to those obtained by Mackie (1988). In such studies, it is recommended that a plexiglass rack be used to compare the toxic levels of contaminant in both sediments and water in the same culture dish.

Cadmium Uptake

In most treatments, cadmium levels in the water were lower at the end of the 15-day experiment than initial levels (Fig. 1). Very little cadmium moved from the sediments to the water in treatments where cadmium was added to the sediments (Treatments 2, 3, 4, Fig. 1). The small levels of cadmium in natural well water was not significantly different ($p > 0.90$) from the background levels in the reagent blanks.

The background level of cadmium in the pond sediment was high, but extremely variable as the large 95% confidence limits in Fig. 2 indicate. One of the 3 controls containing "clean" quartz sand had a high level of cadmium which resulted in large 95% confidence limits (Fig. 2). In general, cadmium levels in the sediments were lower at the end of 15 days than at the beginning, suggesting that cadmium was mobilized into the water. However, cadmium levels in the water also declined over time (Fig. 1). Since cadmium levels in the clams increased over time (Fig. 3), some of the cadmium lost by the water and sediments was taken up by the clams.

Fig. 3 shows a significant difference in the tissue levels of cadmium between the different treatment containers (2-way ANOVA with interaction, p = 0.001), but no differences between clams held in the water column and those in the substrate (p = 0.58). The interaction between treatment container and location within the treatment was not significant (p = 0.21).

The highest tissue cadmium levels were found in clams in Cd-spiked quartz sand (Treatments 1 & 2, Fig. 3). These two treatments were in the same Duncan's group, while clams from the two Cd-spiked pond sediments and the two control groups were in the second Duncan's grouping, as the overlapping 95% confidence intervals in Fig. 3 indicate.

In conclusion, the sphaeriids tested (*Pisidium casertanum*, *Sphaerium rhomboideum*) do accumulate and tolerate the levels of cadmium currently in the environment. Single specimens of most species of *Pisidium* and *Sphaerium* are large enough to provide adequate tissue sample for cadmium concentrations in clams. The sphaeriids do not exhibit a correlation between their tissue cadmium levels and the cadmium levels in the surrounding sediment but apparently take up cadmium from the water and sediments at similar rates, at least when the sediment consists of quartz sand.

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Table 1. Survival and growth of newborn clams in treatments with different substrates and food. All values are percentages. Growth is % of average adult size in natural habitat, where Pc, *Pisidium casertanum* = 3.5 mm; Ms, *Musculium securis* = 6.0 mm; So, *Sphaerium occidentale* = 6.5 mm; Sr, *Sphaerium rhomboideum* = 12.0 mm.

Substrate Type Quartz sand:Pond soil	**Food Materials**	**Survival**				**Growth**			
		Pc	Ms	So	Sr	Pc	Ms	So	Sr
100:0	Tetramin	80	70	50	100	3.0	5.0	4.5	0
75:25	fish food broth	25	70	70	80	5.0	2.0	0	0
50:50	-	0	60	80	30	0	0	0	0
25:75	-	0	70	60	10	0	5.0	1.0	0
0:100	-	0	70	90	20	0	3.5	5.0	0
100:0	Marine	66	0	10	50	3.0	0	0	1.5
75:25	Invertebrate diet	40	10	0	25	2.5	0	0	0
50:50	-	0	25	0	10	0	0	0	0
25:75	-	0	25	0	10	0	0	0	0
0:100	-	0	75	0	0	0	0	0	0
50:50	Trout food broth	0	-**	-	0	0	-	-	0
50:50	*C. emersonii*	100	-	-	100	25.3	-	-	15.7
50:50	*S. capricornutum*	75	-	-	75	6.0	-	-	2.8
0:100*	Willow leaves	80	100	100	50	69.5	80.0	74.3	16.5

* Data for *M. securis* based on Mackie (1979) and for *S. occidentale* on McKee & Mackie (1981).

** - indicates that species was not grown with this food material.

Table 2. Reproduction (average number of newborn per parent//culture dish) four species of fingernail clams raised in laboratory growth dishes in relation to that in their natural habitat (average number of newborn per parent).

Substrate Type	**Food Materials**	**Reproduction in Dishes**				**Reproduction in Habitat**			
Quartz sand: Pond Soil		Pc	Ms	So	Sr	Pc	Ms	So	Sr
100:0	Tetramin	0.3	0	0	0.2	5.5	2.8	3.2	3.1
75:25	fish food broth	0	0	0	0				
50:50	"	0	0	0	0				
75:25	"	0	0	0	0				
0:100	"	0	0	0	0				
100:0	Marine	0	0	0	0				
75:25	Invertebrate diet	0	0	0	0				
50:50	"	0	0	0	0				
25:75	"	0	0	0	0				
0:100	"	0.2	0	0	0				
50:50	Trout food broth	0	-**	-	0				
50:50	C. emersonii	0	-	-	0				
50:50	S. capricornutum	0	-	-	0				
0:100*	Willow leaves	0.2	3.2	2.5	0				

* Data for M. securis based on Mackie (1979) and for S. occidentale on McKee & Mackie (1981)
** - indicates that species was not grown on this food material.

Table 3. 96-h acute lethal toxicity of cadmium (mg L^{-1}) to *Pisidium casertanum* in sediments in relation to water (see text for details). 95% confidence interval given in parentheses.

Sediments	Water
0.85 (+/-0.28)	0.75 (+/-0.31)

CAPTIONS TO FIGURES

Fig. 1. Cadmium concentrations in soft tissues of *Sphaerium rhomboideum* after 15 days in six different treatments of cadmium-spiked well water, unspiked well water, cadmium-spiked quartz sand or pond sediments and unspiked quartz sand or pond sediments. Vertical lines are 95% confidence intervals based on 5 clams in each of 3 dishes (i.e. 15 clams).

Fig. 2. Cadmium concentrations in water after 15 days in six different treatments of cadmium-spiked well water, unspiked well water, cadmium-spiked quartz sand or pond sediments and unspiked quartz sand or pond sediments. Vertical lines are 95% confidence intervals based on average concentrations in each of 3 dishes.

Fig. 3. Cadmium concentrations in sediments after 15 days in six different treatments of cadmium-spiked well water, unspiked well water, cadmium-spiked quartz sand or pond sediments and unspiked quartz sand or pond sediments. Vertical lines are 95% confidence intervals based on average concentrations in each of 3 dishes.

Figure 1

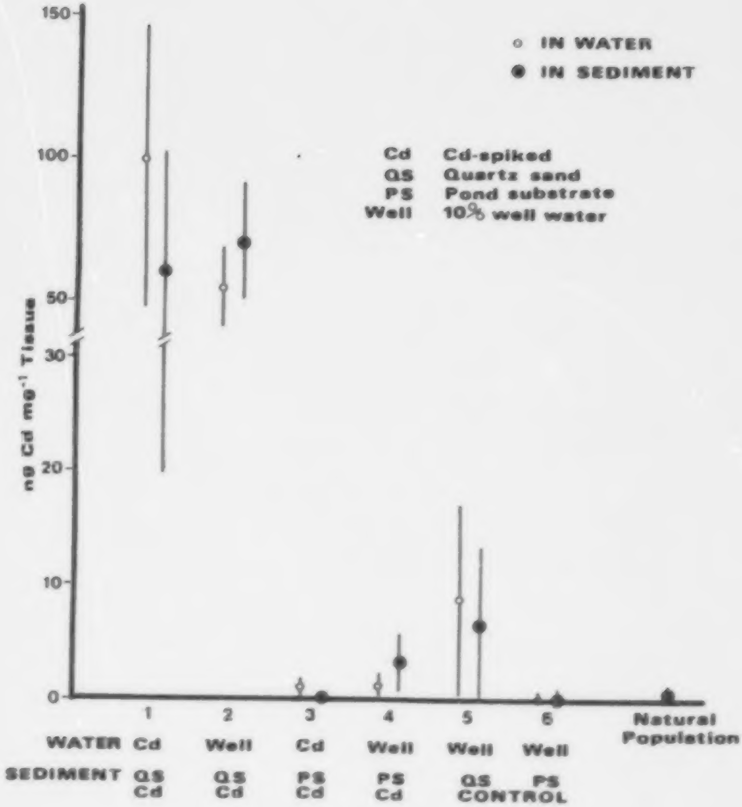

150
100
50
30
20
10
0
ng Cd mg⁻¹ Tissue
○ IN WATER
● IN SEDIMENT
Cd Cd-spiked
QS Quartz sand
PS Pond substrate
Well 10% well water
1
2
3
4
5
6
Natural Population
WATER Cd Well Cd Well Well Well
SEDIMENT QS Cd QS Cd PS Cd PS Cd QS PS
CONTROL

Figure 2

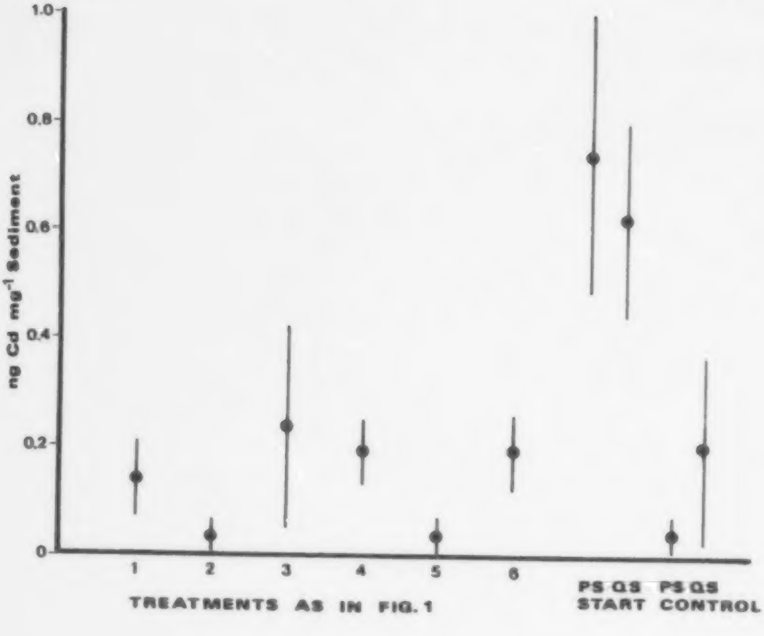
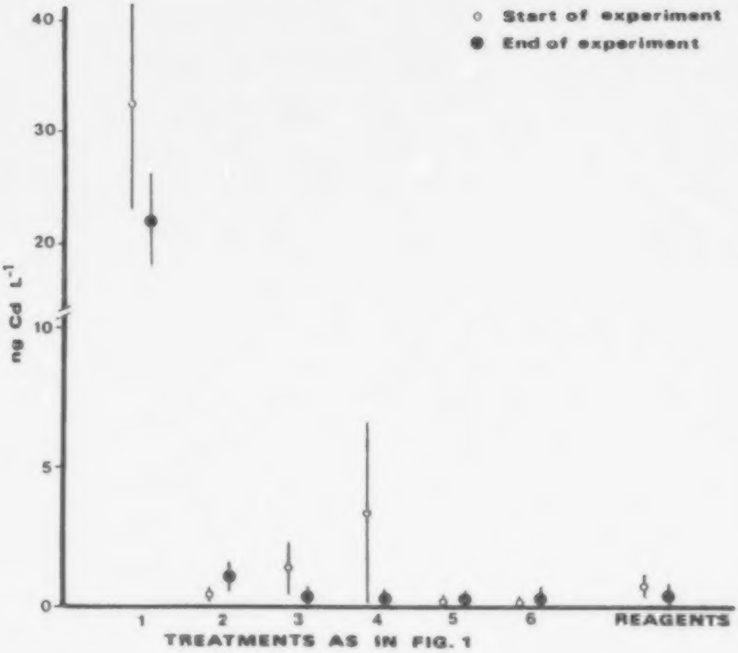

1.0
0.8
0.6
0.4
0.2
0
ng Cd mg^{-1} Sediment
1
2
3
4
5
6
PS QS
START
PS QS
CONTROL
TREATMENTS AS IN FIG. 1

Figure 3



○ Start of experiment
● End of experiment
ng Cd L^{-1}
40
30
20
10
5
0
1
2
3
4
5
6
REAGENTS
TREATMENTS AS IN FIG. 1

B9

RESIDUE-BASED INTERPRETATION OF TOXICITY AND BIOCONCENTRATION QSARs BASED ON AQUATIC BIOASSAYS

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INTRODUCTION

In previous papers it has been established that simultaneous examination of toxicity and bioconcentration QSARs indicates that, for some neutral organic chemicals and some typically employed aquatic test species, 50% mortality in the exposed population occurs at a relatively constant body burden (McCarty, 1986; McCarty, 1987a&b). Although there is a theoretical explantation for this phenomena we wish to determine if it still observed when a larger, more diverse group of organic chemicals is employed. Thus the possibilities of practical exploitation would be improved.

MATERIALS AND METHODS

The main data set is that published by the U.S. EPA's Environmental Research Laboratory-Duluth (Brooke et al., 1984; Gieger et al., 1985, 1986, 1988) employing the fathead minnow (Pimephales promelas) as the test organism. This consists 665 96 hour acute toxicity bioassays on 562 different chemicals. The subset selected for study consisted of 152 tests on 126 different chemicals for the chemical classes: cyclic and non-cyclic halogenated aliphatic hydrocarbons, ethers, simple and halogen-substituted alcohols, ketones, esters and phthalates, and substituted benzenes. Several pesticides were also selected from the anilides and ureas and the other pesticides groups. These chemicals were deliberately chosen on the basis of apparent narcotic mode of toxic action and neutral (non-polar) character. The criteria for narcotic mode of action were: general fit to the neutral, narcotic organics QSAR regression and no ionization as evidenced by lack of an estimate for pKa, the ionization constant. Other criteria included: sufficient data to ensure that a toxicity threshold had occurred (Sprague, 1969) and sufficient mortality data to calculate several LC50 estimates at times less than 96 hours.

A similar comprehensive set of data is not available for bioconcentration in fathead minnows. Fortunately, for the case of neutral, non-metabolised organics the partitioning appears to be a simple steady-state equilibrium between the water and the organism. As proposed by Mackay (1982) the fish typically employed in bioconcentration testing appear to act as a 5% water and lipid solution ie. BCF = Kow*0.48. Call et al. (1980) reported a average lipid content of 4.1% for fatheads of 0.1 to 0.15 g and 8.2% total lipid for larger fish, 0.4 to 0.5 g. Carlson and Kosian (1987) found juvenile fish about 0.1 g in weight were typically between 3% and 4% total lipid. Thus, given the lack of specific information for each bioassay, an approximation mean of 5% total lipid content in juvenile fathead minnows typically employed by the U.S. EPA seems reasonable.

The raw mortality data reported by the U.S. EPA (Brooke et al., 1984; Gieger et al., 1985, 1986, 1988) was employed to calculate all LC50 estimates at exposure times less than 96 h as only the latter was explicitly reported. A micro-computer version of the trimmed Spearman-Karber LC50 estimation procedure (Hamilton 1977, 1978) was used compute over 500 intermediate LC50 estimates.

The exposure time-LC50 estimates for a chemical were fitted to a 1CFOK equation in a manner discussed by McCarty (1987a) which is essentially that discussed by Zitko (1979) and earlier by Matida (1960). The non-linear curve fitting routine in the MS-DOS version of Systat 4.0 (Leland, 1987) was used to carry out the estimation. The solution provides two factors: the elimination rate, k2, and a factor which is (1/Cw*BCF). The latter factor is also equivalent to the threshold LC50 water concentration.

QSAR relationships were examined by linear regression analysis using log Kow and log-transformed toxicity or bioconcentration data. The log Kow values were kindly provided by Dr. S. Broderius of EPA-Duluth from the MED CHEM 3.53 database (which provides a "best" estimate from measured values or, where no measured values are present, calculates a value based on the "fragment" method of Hansch and Leo (1979).

The calculated threshold LC50 value was multiplied by its calculated BCF, assuming 5% lipid content (log BCF = log Kow -1.3) to produce an estimated critical body burden.

RESULTS AND DISCUSSION

Regression analysis indicated that there appeared to be statistically significant relationship between log Kow and body burden (log BB, mmol/L = 0.10*log Kow -0.40, n=152, P <0.0001 for both the regression coefficient and the constant). However, over the approximately 7 orders of magnitude spanned by the hydrophobicity data the body burdens vary less than one order of magnitude, 1.7 to 9.8 mg toxicant per litre of tissue. Thus it is not unreasonable to treat the body burden estimate as a constant. In fact, if the estimates of critical body burdens are calculated from the data for chemicals with log Kow values between 0 and 3.0 (n=83) the slope of the regression equation is not significantly different from a slope of zero. These limits are chosen to reduce the effects of water miscibility at low Kows and the errors encountered at high Kows due to the extremely small amounts of chemical present in the water phase. The toxicity and BCF QSARs along with the estimated body burdens are graphically presented in Figure 1.

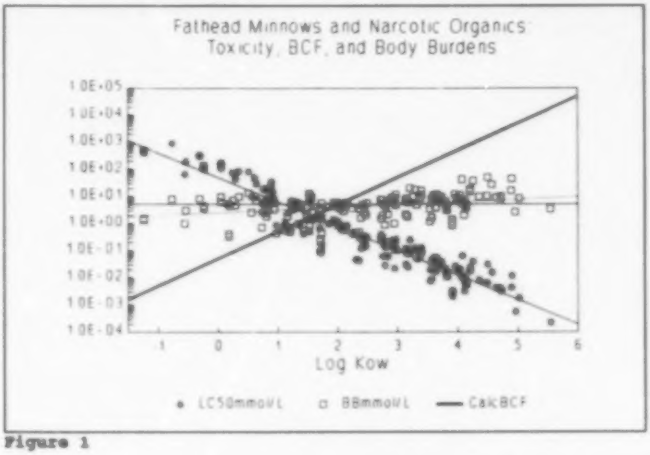

Figure 1

It is difficult to determine a realistic confidence intervals for the critical body burden as the variability of the bioconcentration factor component has not been incorporated into the methodology. Lipid content is not a commonly reported organism characteristic in toxicity testing. As it was not reported in the U.S. EPA-Duluth data set, the variability contributed by experiment to experiment differences in the lipid content of the test organisms can not be investigated and yet lipid content does affect BCF, increased lipid content is associated with increased BCF (Tadokoro and Tomita, 1987).

However, as it is a critical factor in this protocol, sensitivity analysis will be carried out to estimate the influence of lipid content on the critical body burden estimate. The real average total body lipid content of the fathead minnow may not be 5%. Reasonable estimates for a average lipid level could be as low as 3% and as high as 8%. Thus these values were employed in the BCF estimation equation in place of the 5% value. The results are presented in Table 1.

Thus a more realistic estimate of the critical body burden and its variability, especially that due to variations in lipid levels between individuals in the population, would probably be the best estimate of the mean combined with the lower 95 % confidence value of the 3% lipid calculation and the upper value 95 % confidence value of the 8 % lipid calculation. These estimates are 4.3 (2.3-7.4) and 3.1 (1.7-5.6) for the Total data set and the subset (log Kow of 0 to 3) method, respectively. The latter probably represents the best estimate of the lethal body burden for neutral, narcotic organics.

Table 1. Estimated Critical Body Burdens at Various Lipid Levels

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1. 3% Total Body Lipid
   (Total) Critical Body Burden(mmol/L) = 2.6 (2.3-2.8), n = 152
   (Subset) Critical Body Burden(mmol/L) = 1.9 (1.7-2.1), n = 83

2. 5% Total Body Lipid
   (Total) Critical Body Burden(mmol/L) = 4.3 (3.9-4.6), n = 152
   (Subset) Critical Body Burden(mmol/L) = 3.1 (2.8-3.5), n = 83

3. 8% Total Body Lipid
   (Total) Critical Body Burden(mmol/L) = 6.8 (6.3-7.4), n = 152
   (Subset) Critical Body Burden(mmol/L) = 5.0 (4.5-5.6), n = 83

The question arises as to how valid these estimates are when compared to direct observations of molar body burden at death. Although this is not a commonly reported measurement some information is available from the literature for neutral organic chemicals and small aquatic organisms. This is presented in Table 2. The agreement between the information estimated from toxicity and bioconcentration data and that observed is good.

Table 2. Summary of Acutely Toxic Body Burdens From the Literature

Chemical Group	Organism (mmol/kg)	Body Burden	Source
Chlorinated benzenes	Fish	5-12	Carlson and Kosian (1987)
Chlorinated benzenes	Fish	2	Van Hoogen and Opperhuizen (1988)
PCBs	Fish	>0.7	Opperhuizen and Schrap (1988)
Chlorinated benzenes	Insects	3-13	Mclntyre (1988)
PAHs	Crustaceans	4-21	Landrum et al. (1988)
Aminocarb (pesticide)	Fish	1.4-2.3	Richardson and Qadri (1986)
PCBs	Crustaceans	1.4-1.9	Nebeker and Puglisi (1974)
PCBs	Fish	≈ 1	Hattula and Karlog (1972)

Additional support is available from other literature sources. Connolly (1985) indicated that in bioassays with organisms of the same species and condition the molar body burden of the toxicant should be relatively constant for chemicals with a common mode of toxic action. Rogerson et al. (1983) Bobra et al. (1983) reported a constant but unidentified body burden associated with the acute toxicity of hydrocarbons to protozoa. Mackay and Hughes estimated a body toxicant level of 5 mmol/kg for goldfish narcosis. Abernethy et al. (1988) estimated a lethal body burden of approximately 0.006 m^3 toxicant per m^3 tissue.

Since it is usually impractical to quantify the amount of toxicant at the site(s) of toxic action one of the three primary assumptions of toxicology is that the amount of toxicant at the site(s) of toxic action is a function of the amount of chemical to which the organism is exposed. (Timbrell, 1982). Although it is usually the applied or exposure definition of dose that is employed in most toxicological situations, it is clear that, by definition, the effective or target dose, the amount at the site(s) of toxicant action in the organism, is the only correct definition unless the relationship between the exposure and target doses is known. **In essence, if a surrogate for the target dose is to be employed it is crucial that the relationship between the target dose and the surrogate be clearly understood.**

A primary goal of toxicological investigations is: "to know the relative toxicity of the substance with a view to determining its position among other toxic substances whose toxicities are already known" (Filov et al., 1979); in other words to estimate the potency. The key point to be made is that despite the appearance of a number of orders of magnitude difference in the water-borne levels associated with 50% mortality in exposed populations there is NOT a difference in the inherent potency of the chemicals in question, as evidenced by the constant body burden. Thus any water quality criteria based on the exposure water concentrations assuming the differences are potency-related may be suspect. This information also suggests there may be substantial advances to be made by setting criteria for groups of similarly acting chemicals.

Many of the detailed implications, advantages, and applications have been discussed in previous presentations at MOE Technology Transfer Sessions (Mackay et al., 1987; McCarty et al. 1988). The primary goal of this paper was to demonstrate that the concepts apply to a diverse groups of organic chemicals and demonstrate similar trends in independently derived data.

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B10

DEVELOPMENT OF A WATER QUALITY CRITERION FOR THIOCYANATE IN ONTARIO, R.P. Lanno*, S.D. Kevan, and D.G. Dixon, Department of Biology, University of Waterloo, Waterloo, Ontario, N2L 3G1.

Cyanide (CN^-) is used by the mining industry in the extraction and concentration of gold from gold ores. Both froth flotation and leaching utilize CN^- for solubilization and complexation. As a result, cyanides are routinely present in mine effluents in considerable quantities. This situation has long been recognized as an environmental problem and has resulted in the establishment of an Ontario water quality objective for CN^- (0.005 mg/L, as HCN) (Ontario Ministry of the Environment, 1984).

A number of processes have been developed for the elimination of CN^- from gold mine effluents. Cyanide is often complexed with sulphur, either from sulphur dioxide or an inorganic polysulphide, to form thiocyanate (SCN^-). Although SCN^- appears to be much less toxic than CN^-, there is relatively little scientific evidence to fully substantiate this observation. As a result, there is currently no water quality objective for SCN^- in Ontario and no sound data base to establish one.

The 96-h LC50 values for SCN^- for freshwater fish range from 50 to 230 mg/L (Speyer and Raymond, 1985; Doudoroff, 1976), suggesting that SCN^- is substantially less toxic than HCN. Acute toxicity data for SCN^- provides no information on the long-term effects of SCN^- on the growth and reproduction of freshwater fish. Also, the toxic mode of action of SCN^- has not been identified, but often leads to a sudden, violent death termed Sudden Death Syndrome (SDS) by Heming et al. (1985).

The objectives of our research are to obtain sufficient data on the toxicity of episodic exposures of SCN^- to early life stages (ELS) of rainbow trout, and on the long-term sublethal toxicity of SCN^- on the growth, metabolism and reproduction of freshwater fish to permit the development of a water quality criterion.

MATERIALS AND METHODS

The study has been divided into three phases:

1) The long-term sublethal exposure of rainbow trout fry to SCN to determine effects on growth and metabolism

2) A life-cycle study to determine the impact of sublethal SCN exposure on the reproductive capacity of fathead minnows

3) The exposure of ELS of rainbow trout to continuous or pulse-doses of SCN^- (as KSCN or NaSCN).

Acute baseline bioassays

Rainbow trout (2 g) were exposed to various concentrations of SCN^- for a 96 h period, during which mortalities were recorded. At 96 h, fish were stressed by a 15 s pursuit with a hand held dip net, and subsequent mortalities were recorded 30 minutes after the application of the stressor.

Chronic rainbow trout exposure studies

Triplicate groups of juvenile rainbow trout (≈3 g, 55 fish/tank) were continuously exposed to nominal SCN^- concentrations of 40, 80, 120 and 160 mg/L for 16 weeks. Trout were pair-fed a practical trout diet (GRT-70) (Cho et al., 1974). Each treatment tank was randomly matched with a control tank within its block.

Fish were fed ad libitum four times per day, the rations weighed, and an equal weight of food was then fed to the matched control tank for each treatment replicate. Trout were weighed every two weeks to determine growth rates and provide a routine stressor to measure the expression of SDS within each treatment population. Feed intake and mortalities were monitored daily.

At the end of the 16 week growth study, fish were anaesthetized in MS222, killed by cervical dislocation, and length, weight, splenosomatic and hepatosomatic indices, hematocrit, and hemoglobin were measured. Plasma samples for the colourimetric determination of total cyanide-reactive substances (Lambert et al., 1975) and thyroxine (T_4) were obtained by the severance of the caudal peduncle, frozen, and stored at -20°C until analysis. Thyroid, liver, kidney, head kidney, gill, spleen, cartilage and blood smears were sampled from treated and pair-fed control fish, fixed in 10% buffered formalin, and subjected to routine histological observation.

Data were examined for normality and homogeneity of variance by the examination of residuals. One-way ANOVA, using $\log_{10}$ transformed data, was used to determine separately the effects of treatment levels and control food consumption levels on the response variables. ANOVA was then used to detect differences between treatments and their matched controls using a repeated measures design.

Fathead minnow reproduction study

Juvenile fathead minnows (≈4 months old) were separated into 15 tanks in groups of 10 fish/tank, and continuously exposed to nominal concentrations of either 0, 1, 8, 18, or 35 mg SCN^-/L (as KSCN). Since no secondary sexual characteristics were evident at the beginning of the exposure period, ten fish were later thinned out to 2 males/4 females per tank. After 3 weeks of exposure, spawning substrates were introduced into the test system.

Development of secondary sexual characteristics and spawning behaviour were monitored. Reproductive parameters (time to first egg production, number of eggs produced, hatchability) and larval survival and incidence of deformities were monitored for a 4-month exposure period after the introduction of the substrates. After 4 months, fish were anaesthetized in MS222, and length, weight, and hematocrit were measured. Fish were then fixed whole in 10% buffered formalin for routine histological observation. The experiment was just recently completed, so statistical analysis is not yet complete.

Rainbow trout ELS pulse-exposure studies

The study on the effects of pulse-exposure to SCN^- on the ELS of rainbow trout was divided into three distinct phases:

Phase I: Trout eggs were exposed for 3 h to increasing concentrations of KSCN or NaSCN (25 to 3000 mg SCN^-/L) before water hardening or after a 3 h water hardening period.

Phase II: One, 3-, and 10-d-old alevins were exposed to increasing concentrations of KSCN or NaSCN (90 to 2880 mg SCN^-/L) at various pulse durations up to 96 h in a static renewal system. At the end of each pulse test, live fish were transferred to control water and additional mortalities were recorded up to 60 h.

Phase III: Juvenile trout (≈0.6 g) were exposed to SCN^-

Oconcentrations ranging from 0 to 2700 mg/L for pulses of 3, 6, 9, 12, 24, 48, or 144 h. At the end of each test, live fish were transferred to control water and additional mortalities were recorded for 24 h after transfer.

RESULTS

Acute baseline bioassay

The 96-h LC50 for unstressed rainbow trout exposed to KSCN was 250 mg/L. When mortalities due to the stress of a 15 s pursuit with a dip net after the 96-h exposure were included in the calculation, the 96-h LC50 was 180 mg/L. All fish that died after application of the stressor exhibited flaring of operculae, extreme muscle contraction resulting in a dramatic curvature and arching of the body, spasms, loss of equilibrium, loss of buoyancy control and changes in pigmentation, all signs characteristic of Sudden Death Syndrome (SDS).

Chronic rainbow trout exposure study

Mortalities

Mortalities increased with SCN$^-$ concentration, with all fish exposed to 160 mg/L dying by 12 weeks, and approximately 40% of the fish exposed to 120 mg/L dying by the end of the growth trial. SDS was apparent at the two highest concentrations of SCN$^-$, with varying proportions of the population at each treatment expressing SDS after weighing. Mortalities at 40 or 80 mg/L were minimal, except for one replicate (80 mg/L) which was situated near a corner of the experimental system, often being disturbed by laboratory traffic. No occurrence of SDS was observed at the two lowest levels of SCN$^-$ exposure.

Gross physical observations

Cranial deformities were expressed to a varying degree in all trout exposed to SCN^-, the severity of deformity increasing with SCN^- concentration. This condition was characterized by the small size of the head of the trout in relation to the body. Operculae were often shortened or crumpled, exposing gill filaments. Pigmentation changes were apparent as the transitory darkening of individual fish within tanks receiving thiocyanate.

Physiological parameters

Hepatosomatic (HSI) and splenosomatic (SSI) indices were significantly lower in exposed fish (HSI, P=0.0001; SSI, P=0.0006) relative to controls. HSIs decreased with increasing SCN^- concentrations (P=0.0334), but no dose response was apparent for SSIs (P=0.3311). Condition factor was not different between controls and treatment means (P=0.3107) and was not affected by SCN^- level (P=0.5303).

Fish exposed to SCN^- developed an anemia characterized by decreases in hemoglobin (Hb) and hematocrit (Ht). Hb and Ht treatment means were significantly lower (Hb, Ht, P=0.0002) when compared to controls. Ht levels showed trends towards decreasing (Ht, P=0.1078) with increased SCN^- concentrations, while Hb levels did not show a dose response (P=0.5669). Plasma total cyanide-reactive substances increased (P=0.0106) with waterborne SCN^-, while plasma T_4 levels were lower (P=0.0284) in treated fish compared to controls and no dose response was apparent (P=0.67), due to the high variability between tanks within treatments (P=0.0421).

Histology

Histological changes were most prominent in the thyroid, with hypertrophy and hyperplasia of the thyroid follicular epithelium in all fish exposed to SCN⁻. The number of follicles present in treated fish increased when compared to controls. The changes affecting the thyroid can be best characterized as "diffuse hyperplastic goitre". Control fish had low numbers of large follicles, most filled with eosinophilic colloid, and lined by a low cuboidal or squamous epithelium.

Fathead minnow reproductive study

This study was just recently completed and statistical analysis of data is currently underway. The most marked effect of SCN⁻ exposure on maturing juvenile fathead minnows was the delay or lack of development of secondary sexual characteristics and normal spawning behaviour. Fish exposed to 35 mg SCN⁻/L did not develop any secondary sexual characteristics or show any spawning behaviour, not even orientation towards the substrate. Some of the male fathead minnows exposed to 18 mg SCN⁻/L developed the dark stripes and dorsal fin spot characteristic of the species, but failed to develop the large fat pad of actively spawning fish. These males were aggressive towards other fish, but exhibited no herding of females or orientation towards the substrate. Fish exposed to 1 or 8 mg SCN⁻/L fully developed sexual characteristics and followed normal patterns of courtship and spawning, but fish exposed to 8 mg/L produced few eggs. At 1 mg/L, numbers of eggs produced did not appear to differ from controls, but eggs from females in one tank produced a low percentage of non-viable offspring with spinal curvatures.

Mortalities were only apparent at 35 and 18 mg/L with 70% and 30% dying, respectively. Feeding response also appeared to be diminished at 35 mg/L. Fathead minnows exposed to 8, 18, or 35 mg SCN^-/L appeared to develop goitres which protruded from the isthmus behind the lower jaw of the fish.

Rainbow trout ELS pulse-exposure studies

Phase I: Exposure to a 3 h pulse of SCN^- adversely affected the survival and development of rainbow trout eggs before and after water hardening. The NOEC for egg mortality was <650 mg/L for KSCN before water hardening and <1290 mg/L for NaSCN. Hatched alevins exhibited deformities significantly different from controls at concentrations ≥1240 mg/L for all groups tested. Fertilization rates were reduced in eggs exposed to 2900 mg SCN^-/L.

Phase II: The 96 h LC50s for 1- and 10-d-old alevins exposed to KSCN of NaSCN ranged from 191 to 250 mg SCN^-/L, while the 96 h LC50 for 3-d-old alevins was 115 mg SCN^-/L. Mortality did not appear to differ between continuous and pulse-exposure regimes after 48 h. Stress-induced mortality after SCN^- exposure increased at pulses of 48 h or greater, but no signs of SDS were observed.

Phase III: Mean 144 h LC50s for KSCN and NaSCN to juvenile rainbow trout were 149 mg/L and 85 mg/L, respectively, with no acute mortality occurring after 48 h. The application of a stressor after the toxicant exposure period resulted in additional mortality, with the expression of SDS. The LOEC for any ELS tested was 76 mg/L, the 168 h LC50 for trout exposed to stress and NaSCN.

DISCUSSION

The major consequences of the chronic sublethal exposure of rainbow trout to SCN^- are changes in thyroidal morphology characterized by a diffuse, hyperplastic goitre, decreased plasma T_4 levels, deformities in the cranial cartilage, and an anemia characterized by reduced hemoglobin, hematocrit, and splenosomatic indices. Long-term exposure to SCN^- resulted in the development of overt goitre and reduced the expression of secondary sexual characteristics, spawning behaviour, and egg production in fathead minnows. The no observed effect concentration (NOEC) for egg production and spawning behaviour was between 1 and 8 mg SCN^-/L. Fish exposed to ≥ 8 mg SCN^-/L also exhibited signs of overt goitre. The most sensitive ELS indicator of SCN^- toxicity appears to be acute lethality, with a 168 h LC50 of 76 mg/L for juvenile rainbow trout exposed to NaSCN.

The most important effect of SCN^- may be its adverse effect on the thyroid gland (Yamada, et al., 1974; Wood, 1975). Observations on the antithyroidal effects of SCN^- have been almost entirely derived from mammalian research. Elevated plasma SCN^- levels inhibit the uptake of iodine from plasma by the thyroid (Singh et al., 1977), from the water across fish gills (Heming et al., 1985), and possibly from the food. Due to the reduced availability of iodine and possible interferences in the production of T_3 and T_4, negative feedback on the pituitary results in the stimulation of Thyroid Stimulating Hormone (TSH) production. TSH acts upon the thyroid follicular cells to incorporate more iodine for thyroid hormone production. The net result is often seen as goitre, the hypertrophy and/or hyperplasia of the follicular cells of thyroid follicles. Due to the metabolic demand on pituitary for the synthesis of TSH, a reduction in the production of other pituitary hormones may result. A reduction in Gonadotropic Hormone (GTH) may result in reduced reproductive efficiency, as seen with fathead minnows in our study, but the exact mechanism of SCN^- effects on reproduction is unknown. The transitory pigmentation changes and cranial deformities seen in trout exposed to SCN^- may also be due to thyroid dysfunction. LaRoche et al. (1966) and Norris (1969) noted a marked retardation of skull growth, flaring and reduction in the size of operculae, and darkened colouration of radiothyroidectomized rainbow trout compared to normal controls.

Sublethal thiocyanate toxicity in rainbow trout and fathead minnows also appears to involve thyroid function, as seen by histological evidence regarding goitre development, reductions in plasma T_3 levels in trout, deformities in cranial cartilage development, and suppression of secondary sexual characteristics and egg production in mature fathead minnows. The dramatic reduction in egg production observed in fathead minnows at SCN^- concentrations between 8 and 1 mg/L appears to be the most sensitive indicator of SCN^- toxicity, and should be taken into consideration in the development of a water quality objective.

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B11

THE USE OF MASS BALANCE MODELS TO ELUCIDATE THE EFFECTS OF IN-PLACE POLLUTION

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INTRODUCTION

Contamination from chemicals released into the environment is a problem confronting numerous systems. Despite the magnitude and pervasiveness of the problem, and the years during which we have been aware of this issue, we still have only a rudimentary understanding of contaminant fate and behaviour.

We do know that many contaminants ultimately concentrate in sediments, particularly the fine-grained sediments of lakes. Whereas it was formerly believed that contaminants in sediments were largely unavailable to systems, it is now clear that contaminants return to the lake, especially as contaminant emissions diminish. This phenomenon has been termed "in-place" pollution. In terms of the Great Lakes, 41 of the 42 areas identified as "Areas of Concern" are considered to have problems involving in-place pollution. To respond to these problems answers are required to questions such as,

a) what is the contribution from in-place pollution to present contaminant levels,
b) over what time span will in-place pollution persist, and
c) what if any remedial actions can be taken.

The objective of this paper is to present an approach for evaluating chemical fate, especially that of in-place pollution. The approach is based on compiling a mass balance model of chemical behaviour and transport for the system of interest. Mass balance models fulfill the dual goals of improving our scientific understanding of systems as well as contributing to regulatory measures.

In the following discussion we describe a system of mass balance models which employ an equilibrium criterion rather than chemical concentration. We then illustrate the use of the model by applying it to a lake in which arsenic (As) is an in-place pollutant, namely Moira Lake in Eastern Ontario.

CRITERIA OF EQUILIBRIUM

Mackay and co-workers have developed mechanistic, mass balance models which employ an equilibrium criterion in place of chemical concentration (Mackay and Paterson 1981, 1982, Mackay et al. 1983a). Several advantages accrue from using an equilibrium criterion: use of a criterion greatly simplifies model development, both conceptually and mathematically, and the criterion clearly indicates the phase into which a chemical will tend to move, just as temperature indicate the phase into which heat will tend to move.

For chemicals that partition between air and water, fugacity, f (Pa), is used as the equilibrium criterion:

$$f = C\,Z \qquad (1)$$

where C is concentration (mol/m3) and Z is a "fugacity capacity" ($mol/m^3.Pa$). Whereas f expresses the "escaping" tendency of the chemical from a medium, Z quantifies the affinity of that medium for chemical. The ratio of two Z values in phases 1 and 2, Z_1/Z_2, is equal to the partition coefficient K_{12}. To calculate Z values in all media, the Z value for air, Z_A is first calculated:

$$Z_A = 1/RT \qquad (2)$$

where RT is the gas constant temperature group (Pa.m³/mol). The Z value for water, Z_W is then calculated as:

$$Z_W = Z_A/K_{AW} \qquad (3)$$

where K_{AW} is the air-water partition coefficient. Subsequent Z_i values are obtained by multiplying partition coefficients, K_{iW} by Z_T.

This formulation has proved useful for modelling the behaviour of organic contaminants which partition between air and water, i.e. contaminants that are volatile (e.g. Holysh et al. 1986, Mackay 1989). Fugacity is however, inconvenient for nonvolatile chemicals such as metals, metalloids and polymers. For these chemicals we have introduced a water-based equilibrium criterion, "equivalent aqueous" concentration or "aquivalence" (Mackay and Diamond 1989). Similar to the fugacity formulation, concentration is linearly related to aquivalence, A (mol/m³), through a chemical capacity term or Z value:

$$C = A\ Z \qquad (4)$$

By definition, Z_W is established as 1, and subsequent Z values are then equal to dimensionless partition coefficients, K_{iW}.

Using either the fugacity or aquivalence formalisms, all expressions of chemical transport and transformation are expressed in common units as D values. The rate of chemical movement, N (mol/h) then becomes:

$$N = D\ f = D\ A \qquad (5)$$

The units of D are mol/h.Pa for fugacity and m³/h for aquivalence. D values can be defined from mass flow rates (m³/h), mass transfer coefficients (m/h), diffusivities (m²/h) or first order rate constants (h^{-1}). D values for all processes can be linearly added, grouped and compared. Thus, the relative importance of disparate processes such as atmospheric deposition or chemical degradation, becomes immediately apparent. A more complete discussion of this approach has been presented by Mackay and Diamond (1989).

THE WHOLE LAKE MODEL

The model used to describe chemical dynamics in a lake derives from the QWASI model (Quantitative Air Water Sediment Interaction, Mackay et al. 1983b). The system consists of two well mixed compartments, the water column and an active layer of sediments (Figure 1, Diamond 1989). In both compartments chemical partitions between dissolved (aqueous or pore water) and sorbed (suspended particle or solid sediment) phases. Chemical can enter the system through wet (D_C) and dry (D_Q) deposition, rain dissolution (D_M), and advective flow of water (D_I) and suspended particles (D_X). Chemical is lost from the system by advective flow of water (D_J) and particles (D_Y), solid sediment (D_B) and pore water (D_L) burial. Chemical can exchange between water and sediments as a result of sediment deposition (D_D) and resuspension (D_R), bidirectional diffusion (D_T) and pore water irrigation (D_S).

Equating chemical inputs and outputs, the general steady state mass balance equation for the water column is:

$$A_A(D_Q+D_C+D_M) + A_I(D_I+D_X) + A_S(D_R+D_T+D_S) = A_W(D_J+D_Y+D_D+D_T+D_S) \quad (5)$$

and for the sediments is:

$$A_W(D_D+D_T+D_S) = A_S(D_R+D_T+D_B+D_S+D_L) \qquad (6)$$

where the subscripts A, I, S and W refer to air, inflow, sediments and water, respectively. Equations (5) and (6) can be solved analytically for steady state conditions. To run the model values of A_A and A_I must be specified as well as all D and Z values.

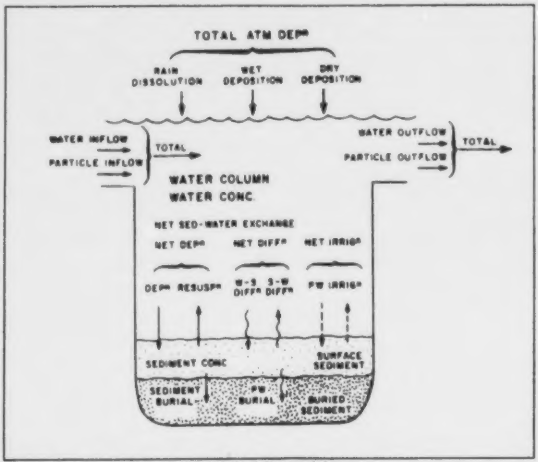
TOTAL ATM DEPⁿ
RAIN DISSOLUTION
WET DEPOSITION
DRY DEPOSITION
WATER INFLOW
PARTICLE INFLOW
TOTAL
WATER OUTFLOW
PARTICLE OUTFLOW
TOTAL
WATER COLUMN
WATER CONC.
NET SED-WATER EXCHANGE
NET DEPⁿ
NET DIFFⁿ
NET IRRIGⁿ
DEPⁿ
RESUSPⁿ
W-S DIFFⁿ
S-W DIFFⁿ
PW IRRIGⁿ
SEDIMENT CONC
SURFACE SEDIMENT
SEDIMENT BURIAL
PW BURIAL
BURIED SEDIMENT

Figure 1. Illustration of the whole lake model.

LINEAR ADDITIVITY PRINCIPLE

In many circumstances, especially those involving in-place pollution, it would be useful to quantify the amount of chemical attributable to a particular source, and to distinguish that contribution from the total system behaviour. The Linear Additivity Principle (LAP) of Stiver and Mackay (1989) can be used for these purposes. The LAP asserts that the net behaviour of a chemical in a system is the sum of behaviours attributable to individual chemical sources. These sources may vary in time and/or space. For the LAP to apply, the model must be linear, i.e. all expressions describing partitioning, transformation and transport must be first order with respect to concentration, as in the fugacity/aquivalence models.

If individual contaminant discharges behave independently of one another, as demonstrated by Stiver and Mackay (1989), then the behaviour attributable to a specific source can be subtracted from the net chemical behaviour. The LAP can also be used to determine the contribution of chemical from an unknown source as the difference between observed chemical values and model estimates of the sum of all known chemical sources. In particular, contributions from in-place pollution can be deduced by comparing observed chemical concentrations in all media with steady state model estimates.

APPLICATION OF THE MODEL

Moira Lake, located on the Moira River which discharges into Lake Ontario at Belleville, was selected to demonstrate the aquivalence-based whole lake model and use of the LAP (Diamond et al. 1987). Moira Lake is a shallow, softwater, eutrophic lake comprised of three distinct basins of increasing size, Bend Bay, West Basin and East Basins (Figure 2). Since 1866, As has been entering the Moira River 21 km upstream of Bend Bay at Deloro, the site of mining and mineral processing activities until 1961.

The model of average annual conditions in Moira Lake was parameterized and calibrated with data obtained from year-round field studies conducted from 1986 to 1988, government monitoring

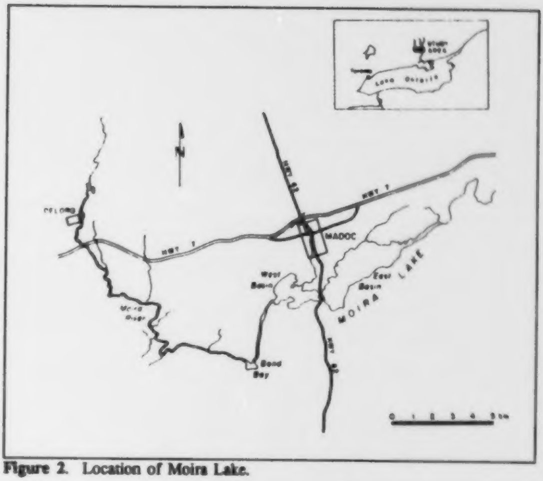

Figure 2. Location of Moira Lake.

data and the literature. Values used in the model and details of the calibration procedures are presented in Diamond (1989).

To determine the contribution of past As loadings that have accumulated in the sediments, the model was run with an average annual inflow concentration of 30 ug As/L (typical concentrations in uncontaminated systems range from 1 to 5 ug As/L) and observed sediment concentrations of 900, 600 and 650 ug As/g in Bend Bay and West and East Basins, respectively. These inflow and sediment concentrations correspond to conditions from 1985 to 1988. Specifying sediment concentrations was necessary because they are the result of past loadings and as such can not be predicted from current steady state conditions.

Results from the model simulation illustrate the high mobility of As in Moira Lake (Figure 3). Arsenic, which is approximately 85% dissolved, is conveyed by advective flows and exchanges between the sediments and water by, primarily, deposition of particle-sorbed As, dissolution in the sediments and sediment-to-waterdiffusion of dissolved As. Advection becomes less important and sediment-water exchange becomes more important with increasing basin size (and coincidentally, downstream direction). Atmospheric deposition to all basins is negligible.

These results approximate current conditions in Moira Lake. The estimated concentrations and rates of chemical movement are the sum of a steady state contribution from present sources (inflow and atmospheric deposition) and an unsteady state contribution from As accumulated in the sediments. The unsteady state contribution can be uncoupled from the total behaviour by subtracting model estimates obtained from specifying the inflow concentration alone, from estimates obtained from specifying the inflow and sediment concentrations. This can be done for each basin individually to estimate basin-specific contributions, i.e. the downstream propagation of As.

This analysis suggests that 66, 35 and 22% of As in the sediments of Bend Bay and West and East Basins, respectively, is attributable to present As inputs (river inflow and atmospheric deposition), with the remainder being the "in-place" or unsteady state portion, attributable to past sources. Of the estimated 5540 kg of As in East Basin water and active sediments, 1% originates

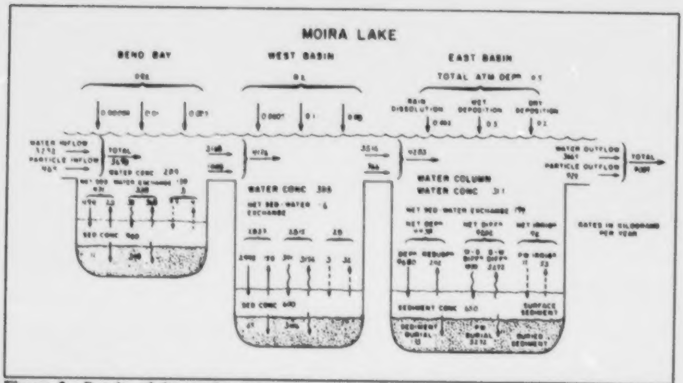
MOIRA LAKE
BEND BAY
WEST BASIN
EAST BASIN
TOTAL ATM DEP
RAIN DISSOLUTION
WET DEPOSITION
DRY DEPOSITION
WATER INFLOW
PARTICLE INFLOW
TOTAL
WATER CONC
NET BED-WATER EXCHANGE
BED CONC
WATER COLUMN
WATER CONC
WATER OUTFLOW
PARTICLE OUTFLOW
TOTAL
RATES IN KILOGRAMS PER YEAR
SEDIMENT CONC
SURFACE SEDIMENT
SEDIMENT BURIAL
BURIED SEDIMENT

Figure 3. Results of the steady state model of Moira Lake simulating average annual conditions in 1985 to 1988.

from Bend Bay, 10% from West Basin and 64% from accumulation in East Basin sediments. Thus, whereas 66% of As in Bend Bay water and active sediments is from present inflows, only 25% of As in east Basin is from present sources. Contributions from all basins to total As movement in East Basin are illustrated in Figure 4.

DISCUSSION AND CONCLUSIONS

The modelling approach discussed herein, is believed to be simple and general. These attributes apply to the equilibrium criteria (fugacity for volatile chemicals and aquivalence for nonvolatile chemicals), expression of all transport and transformation processes by D values, and use of the LAP to uncouple contributions from various chemical sources. That the simple and general nature of the approach do not slip into the trivial, is ensured by the sound mechanistic basis of the mass balance model, from both chemical and limnological perspectives. Thus, the approach demonstrated here in one lake can be extended to most systems provided that there is knowledge of system-specific parameters (e.g. sediment deposition and resuspension rates), and to most chemicals given knowledge of its physical-chemical properties (e.g. vapour pressure and solubility for organic chemicals, K_p values for inorganic chemicals). Indeed, this has been done with models of PCBs and lead in Lake Ontario (Mackay and Diamond 1989).

In terms of in-place pollution, we can answer the questions posed in the Introduction, or more specifically estimate contributions from in-place and current sources, by using the whole lake model in conjunction with the LAP of Stiver and Mackay (1989). For Moira Lake, we have estimated that 78% of current sediment concentrations and 57% of current water concentrations in East Basin, are attributable to in-place pollution. The time required for these contributions to dissipate is believed to be short due to the rapid movement of As in the system.

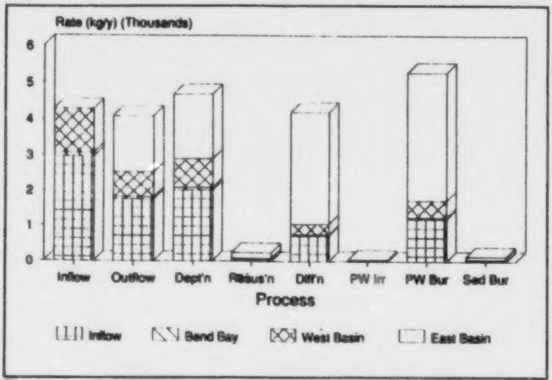

Figure 4. Contributions to As movement in East Basin from present and accumulated sediment sources in each basin as deduced from the Linear Additivity Principle.

Our current work is devoted to providing well documented case studies using this approach, such as Moira Lake, and more recently the Bay of Quinte. We believe that simple mass balance models can play a very useful role in elucidating the dynamics of chemicals in situations of in-place pollution and thus contributing to more effective remediations.

ACKNOWLEDGEMENTS

This research was funded by the Ontario Ministry of the Environment at the recommendation and subsequent supervision of Deo Persaud. Glenn Owen and members of the Southeastern Branch of the Ministry generously gave of their time, expertise and data. Dr. Sheldon Landsberger of the University of Illinois performed all As analyses. Daniel Phalp, Gus Cheng, Denis Limin, Mel Martin and Carol Ann Kramp ensured the success of field and laboratory work.

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B13

REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO, 1960 TO 1985

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INTRODUCTION

The discovery, in August, 1985, of the highly publicized chemical "BLOB", 54 tonnes of perchloroethylene, in the St.Clair River adjacent to the Dow Chemical facility near Sarnia, Ontario caused considerable anxiety in Kent and Lambton Counties. The public became concerned that the consumption of drinking water from the river might have resulted in increased rates of cancer, abnormal outcomes of pregnancy and infant deaths. This study was designed to determine if increased rates of the latter two conditions had occurred in the two counties over the six year period, 1980 through 1985, and if so, whether they were associated with the consumption of drinking water from the St.Clair River.

METHODS

The study was conducted in three phases. First, births to mothers resident in Wallaceburg and Tilbury, the two major centres which draw their drinking water from the river, were designated as exposed. Those from the remainder of Kent were classed as nonexposed. The total (six year) incidence rates of spontaneous abortion, stillbirth, congenital anomalies, low birth weight, early and total neonatal deaths, perinatal deaths and infant deaths were calculated for the exposed and nonexposed groups of Kent County and for Lambton County. The incidence rates were compared with those of the Ontario Southwest Region (OSWR)[1] including and excluding the two counties and with the rates of the Province (ON) including and excluding Kent and Lambton.

Second, attempts were made to trace and interview at home all women in the two counties whose pregnancies had resulted in stillbirths, congenitally anomalous babies, babies weighing equal to or less than 1,500gm. at birth or whose children had died before twelve months of age during the period of study, the cases. A matched control group of women whose pregnancies had normal outcomes and whose children survived the first year of life was also interviewed. The groups were matched on county of residence, date of birth (± 60 days), maternal age (± 1 year), parity (± 1) and sex of the child. The interview covered sociodemographic variables, occupation, health and medical conditions during the index pregnancy, personal habits, histories of previous and subsequent pregnancies and, most important, source and amount of water consumed. To detect an association between the adverse outcomes and St.Clair River drinking water, the frequencies of exposure of the cases were compared with those of the matched control group.

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[1] The Ontario Southwest Region includes : Bruce, Elgin, Essex, Grey, Huron, Kent, Lambton, Middlesex, Oxford and Perth Counties.

Third, the timing of five specific chemical spills into the river and place of residence were used to define a group of women whose pregnancies were at risk of exposure. A second group of women, resident in the same areas, but whose pregnancies occurred at times other than the chemical spills was also assembled. The third group investigated consisted of women resident in other areas of Kent County whose pregnancies occurred at the same time as those of the first group. This latter group was matched with women of the first group on maternal age (± 1 year), parity (± 1) calculated date of last menstrual period (± 60 days) and date of birth of the child (± 60 days). The women in the first two groups were interviewed by telephone to confirm their exposure, or lack thereof, to drinking water from the St.Clair River and to determine relevant details of the index, previous and subsequent pregnancies. A similar interview was conducted with a random sample of the women in the third group. The total (six year) incidence rates of stillbirth, congenital anomalies and low birth weights ($\leq$ 1,500g) of the exposed group were compared with those of the two nonexposed groups.

RESULTS AND DISCUSSION

With the exception of spontaneous abortion (Table 1) and stillbirth (Table 2), the incidence rates of all of the other abnormal outcomes of pregnancy and infant deaths did not differ significantly from those of the OSWR or ON. The rates of

Table 1. Total incidence and relative risks[1] of spontaneous abortion, Kent and Lambton Counties, 1980 through 1985.

AREA	RATE[2]	RISK	LIMITS[3]
OSWR[4]	45.2	--	----
Kent County			
Exposed[5]	64.0	1.42*	1.20-1.68
Nonexposed	76.2	1.96*	1.56-1.83
Total	73.9	1.64*	1.53-1.76
Lambton County	24.4	0.54*	0.18-0.61

[1] Ratio of the incidence rates of Kent and Lambton counties to that of OSWR.

[2] Rate per 1,000 pregnancies (total births plus spontaneous abortions).

[3] 95% confidence limits of the risk estimates.

[4] The Ontario Southwest Region.

[5] Wallaceburg and Tilbury.

* Significantly different from 1, $P < 0.05$.

spontaneous abortion in Kent County as a whole and those of the exposed and nonexposed subgroups were all significantly higher than that of the surrounding population. In addition, the rate in the nonexposed group was some 19 per cent higher than that of the exposed group, a difference which bordered on statistical significance. Conversely, the rate of spontaneous abortion in Lambton County was significantly below expectation.

Table 2. Total incidence and relative risks[1] of stillbirth,
Kent and Lambton Counties, 1980 through 1985.

AREA	RATE[2]	RISK	LIMITS[3]
OSWR[4]	6.6	--	----
Kent County			
Exposed[5]	2.7	0.40*	0.17-0.96
Nonexposed	7.6	1.15	0.89-1.49
Total	6.7	1.01	0.79-1.30
Lambton County	6.2	0.93	0.73-1.18

[1,3-5,*] See footnotes, Table 1.
[2] Rate per 1,000 total births.

The rates of stillbirth in Kent and Lambton Counties as a whole were almost identical to that of the OSWR. However, the exposed group in Kent County had a rate which was significantly lower than those of both the OSWR and the nonexposed group.

The results of this ecologic phase of the study did not support an association between the St.Clair River as a source of drinking water and the adverse reproductive and first-year-of-life outcomes investigated. The rates of occurrence of most of the events did not differ significantly from those of the OSWR or ON. The significantly high incidence rate of spontaneous abortion in the exposed group may, at first glance, point to an effect of the river. However, this interpretation is negated by the observation of an even higher rate in the nonexposed group. The significantly low rate of stillbirth in the exposed group also argues against a toxic effect of drinking water because it would not be expected to exert a protective effect.

The study group for the case-control study consisted of 489 pregnancies which resulted in 441 abnormal outcomes of pregnancy and 192 infant deaths. We were able to trace and interview 309 mothers of cases, a response rate of 63 per cent. A like number of controls were also interviewed giving a total sample of 618. The untraceable subjects and nonrespondents did not differ significantly from the respondents providing some assurance that the missing subjects did not introduce bias into the results.

The case and control respondents showed a high degree of comparability on most of the variables which were examined. However, the cases tended to have lower family incomes and less education. More were current cigarette smokers and reported smoking and having an ultrasound examination during the index pregnancy. Fewer of them reported their health as excellent or good during their pregnancies.

The results of the matched pairs analysis of the relationship between home water source and the outcomes of interest are shown in Table 3. All of the odds ratios indicated no significant case-control differences in the frequencies of exposure to St.Clair River drinking water at home. Similarly negative results were obtained in the comparisons of water sources at work and at home and/or at work. Because this was a population based case-control study, it was possible to estimate incidence rates in the exposed and nonexposed groups and to calculate relative risks. They were 0.95, 0.64, 0.90, and 0.91 for stillbirths, congenital anomalies, low birth weight and infant deaths respectively. None differed significantly from 1.

Table 3. Matched pairs analysis of the association between St.Clair River water as the source of drinking water at home and abnormal outcomes of pregnancy and infant deaths, Kent and Lambton Counties, 1980 through 1985.

OUTCOME	NUMBER OF PAIRS	ODDS RATIO[1]	LIMITS[2]
Stillbirths	69	1.00	0.48-2.23
Congenital anomalies	83	0.64	0.35-1.30
Birth weight ≤1,500g	104	1.00	0.51-2.08
Infant deaths	92	1.00	0.54-1.98

[1] An odds ratio = 1 indicates no association.
[2] 95% confidence limits of the estimated odds ratio.

This case-control analysis provided no more support for the hypothesized association between reproductive outcomes and infant deaths and St.Clair River water than did the previous ecological analysis. Since bias and confounding could be ruled out as explanations for the results, the findings suggest that no real difference existed between the cases and controls regarding their exposure to river water.

The chemical spills which were selected for the third phase of the study are listed in Table 4. The criteria for selection were: the timing of the spills, the chemical involved, the amount spilled and the amount recovered. The definition of the exposed cohort of pregnancies was based on the time of the spills and women who were up to eight months pregnant or conceived within one month of each spill. This procedure gave periods at risk of exposure as follows: 18 January to 8 November, 1980; 31 December, 1981 to 21 October, 1982; 3 March to 28 December, 1984; and 25 August, 1985 to 7 January, 1987. The last period consisted of two different spills, one of which occurred in August, the other in December, of 1985.

Table 4. Chemical spills into the St.Clair River designated as exposures, 1980 through 1985.

DATE	CHEMICAL	AMOUNT metric tons	RECOVERED per cent
80-01-08	Bunker C oil	21	38
81-12-21	Bunker C oil	21	81
84-02-22[1]	No.2 oil	116	80
84-02-27	No.2 oil	16	81
85-08-13 to 16	Perchloroethylene[2]	54	100
85-12-19	Isobutylene wash water	26	0

---

[1] Since these spills were close in time and of the same chemical, they were considered as one spill.

[2] The infamous "BLOB".

The numbers of births which occurred in the exposed and nonexposed cohorts in the four time periods are shown in Table 5.

Table 5. Numbers of births during the periods of interest, Kent County.

COHORT	NUMBERS Livebirths	 Stillbirths	TOTAL
Exposed	1,656	5	1,661
Nonexposed[1]	866	2	868
Nonexposed[2]	4,075	23	4,098

---

[1] Pregnancies occurred in the exposed areas at times other than the spills.

[2] Pregnancies occurred outside the exposed areas at the times of the spills.

In only one instance, the comparison of stillbirth rates between the exposed cohort and women living in the same areas whose pregnancies were not exposed to the spills, did the relative risk exceed 1 and it was statistically nonsignificant (Tables 6-8). In all of the other comparisons, the rates in the exposed cohort were lower than those of the nonexposed, significantly so in three cases.

These results indicated no association between the specific chemical spills and the occurrence of stillbirth, congenital anomalies and low birth weight babies. If the spills had been affecting the reproductive outcomes, we would have expected to see increases in the rates in women who were exposed at these times. The converse was the case. The reason for this observation is unclear. The play of chance on relatively rare events in small populations may be the explanation.

SUMMARY

This epidemiologic study was designed to evaluate the possible association between the consumption of drinking water from the St.Clair River and abnormal outcomes of pregnancy and adverse first-year-of-life outcomes. It consisted of an ecologic analysis, a case-control comparison and a retrospective cohort study. None of the analyses provided support for the hypothesized relationship. The results indicated that St.Clair River water consumption was not associated with increased rates of the the adverse outcomes studied.

Table 6. Total incidence of stillbirth in the exposed and nonexposed cohorts, Kent County.

Cohort	Number	Rate[3]	Relative risk[4]	Limits[5]
Exposed	5	3.01	--	--
Nonexposed[1]	2	2.30	1.31	0.25-6.75
Nonexposed[2]	23	5.61	0.54	0.20-1.42

[1,2] See footnotes, Table 8.

[3] Rate per 1,000 total births.

[4] Risk in the exposed relative to the nonexposed.

[5] 95% confidence limits of the risk estimate.

Table 7. Total incidence of congenital anomalies in the exposed and nonexposed cohorts, Kent County.

Cohort	Number	Rate[3]	Relative risk[4]	Limits[5]
Exposed	4	2.41	--	--
Nonexposed[1]	14	16.17	0.15*	0.05-0.46
Nonexposed[2]	66	16.11	0.15*	0.05-0.41

[1-5] See footnotes, Table 8.1.

* Significantly less than 1, $P<0.05$.

Table 8. Total incidence of birth weights $\leq$1,500gm., in the exposed and nonexposed cohorts, Kent County.

Cohort	Number	Rate[3]	Relative risk[4]	Limits[5]
Exposed	7	4.23	--	--
Nonexposed[1]	10	11.55	0.37*	0.14-0.96
Nonexposed[2]	32	7.85	0.54	0.24-1.23

[1,2,4,5,*] See footnotes, Table 8.2.

[3] Rate per 1,000 livebirths.

B14

File No: C0873108

DEVELOPMENT AND PILOT SCALE DEMONSTRATION OF A POWDERED ACTIVATED CARBON/CROSS FLOW FILTRATION SYSTEM FOR DRINKING WATER TREATMENT

H. Donison, A. Benedek, and J.J. Bancsi, Zenon Environmental Inc.

Powdered activated carbon (PAC) is widely used in Ontario and around the world for the removal of taste and odour from drinking water. More recently PAC has been finding use in the removal of toxic organics from drinking water either in the case of chronic low level contamination or occasional high levels resulting from an accidental spill. ZENON Environmental Inc. has undertaken a study for the Ontario Ministry of the Environment to develop an improved system for the application of PAC in water treatment plants.

At the outset of this study criteria were established to aid in the evaluation of reactor alternatives. The criteria were selected to ensure optimization of the adsorption process and to meet the requirements of the treatment plant operators and the Ontario Ministry of the Environment. The following seven essential criteria were used to evaluate the potential reactor alternatives:

a) The PAC must be in contact with the water for at least one minute to ensure adequate time for adsorption of organic pollutants.

b) The adsorption process should be contact stratified or plug flow to use the carbon efficiently and to produce high quality product water.

c) It is essential that the PAC added is reliably and effectively retained by the reactor to prevent deposition of PAC downstream in the water treatment process or distribution system.

d) The system must be adaptable to existing facilities.

f) The process must operate reliably.

g) The system must be mechanically reliable.

The "desirable" criteria were included in this analysis as conditions which would have benefits for the MOE or treatment plant operators but were not necessary to an improved PAC contactor system. The first desirable criteria was that the system be portable so that it could be moved to a facility encountering temporary contamination problems. The second desirable criteria is that the PAC be recovered in a form suitable for regeneration.

The third class of criteria were the cost criteria which were included to ensure that any system selected for further investigation have reasonable capital, labour and operation and maintenance costs associated with it.

Downflow PAC packed bed filtration and multi-stage crossflow filtration met all of the criteria and were selected for development at bench scale. Figure 1 and Figure 2 are schematic diagrams illustrating these two systems.

In bench scale testing, performance of downflow PAC packed bed filtration was proven to be unreliable due to the development of channels through the bed. Variation of system operation, bed depth and addition of diatomaceous earth to the bed did not overcome this problem.

Crossflow membrane filtration was proven in bench scale tests to effectively separate PAC from an aqueous stream. The separation was 100% with no PAC entrained in the effluent

The membrane process is not essentially contact stratified, however it is suitable for multistage use which approximates contact stratification. Laboratory testing showed that a PAC cake is formed within the membrane tube, which suggested contact stratification. However, further testing proved that the cake is too thin, and the water passes through the cake too rapidly for sufficient contact time for effective contact stratification.

Sufficient contact time can be provided in the recirculation stream for adsorption. The system must be designed and operated such that once the PAC cake has been established, all additional PAC fed to the system remains in suspension in the recirculating stream until it is bled out of the system.

The laboratory testing was completed using Burlington tap water which is typical of finished drinking water from surface sources in Southern Ontario. The system was shown to be effective as a final treatment step and processed water and could be added to existing plants. It is possible that this system would be suitable for the treatment of raw water and could replace conventional treatment. Further testing with a variety of raw water types would be necessary to evaluate this potential.

The PAC/Crossflow filtration (CFF) system would by the nature of adsorption automatically adsorb a contaminant peak. For particularly high peaks the carbon dosage could be increased.

The laboratory scale testing indicated that the process is reliable. The buildup of the PAC cake in the membranes reduced problems due to fouling. Mechanical reliability will depend on the reliability of the sub-components. Sub-components will have to resist abrasion by PAC.

Overall, bench scale tests indicated that the PAC/CFF system held technical promise. Multistage crossflow PAC filtration using a two-stage ultrafiltration tubular system was shown to be technically feasible in the laboratory scale processing. Preliminary estimates show the costs of water production for this system to be $1.83/1000 gallons. This system would be technically and economically competitive with granular activated carbon.

Based on the success of the bench scale tests a pilot scale testing program was undertaken. A pilot scale system was designed and built. The process flow diagram is shown in Figure 3. The pilot system is a portable system suitable for demonstration of the PAC/CFF process for portable water treatment. Since the system is to be used for process development, it is adaptable so that operation conditions can be varied and it has sufficient instrumentation to monitor system performance.

Untreated water is pumped from the source to a raw water reservoir. This reservoir acts as feed tank for feed and bleed operation or a process tank for batch concentration operations. PAC is added as a slurry to the raw water feed stream. The raw water/PAC stream is fed by the process pump to a tubular membrane module and clean permeate produced. The concentrate stream, which contains the PAC is recycled. A small bleed stream containing spent carbon is removed from the recycle loop. The hydraulic retention time in the membrane/recycle loop is approximately five minutes. The option also exists for the PAC containing concentrate stream to be returned to the reservoir and the system operated in a batch concentration mode.

At the time of writing arrangements have been made to demonstrate the pilot system at the Brantford water treatment plant during October and November 1989. The objectives of the demonstration are as follows:

- To optimize PAC/CFF for drinking water treatment and toxic organic pollutant removal.
- To evaluate PAC/CFF as an alternative treatment strategy to that of conventional water treatment for the removal of suspended solids, bacteria and dissolved organic pollutants.
- To directly compare the performance, reliability and cost of PAC/CFF with conventional processes for water treatment at a Southern Ontario water treatment plant.

The key outputs of this demonstration are expected to be:

- produced water quality
- optimum operating conditions

- operating problems
- capital and operating costs for full scale system

A technical and economic evaluation of the PAC/CFF system will be made based on the results of this demonstration.

ACKNOWLEDGEMENT:

We gratefully acknowledge the ongoing advise of Jim Dart of the Ministry and the co-operation of the Brantford Public Utilities in support of this study. This study is funded by the Ontario Ministry of the Environment.

FIGURE 1: DOWN FLOW FILTER

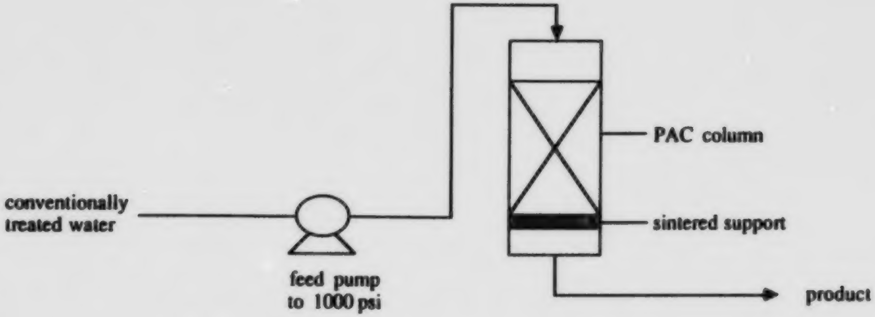

conventionally treated water
feed pump to 1000 psi
PAC column
sintered support
product

FIGURE 2: MULTI-STAGE CROSSFLOW SURFACE FILTER

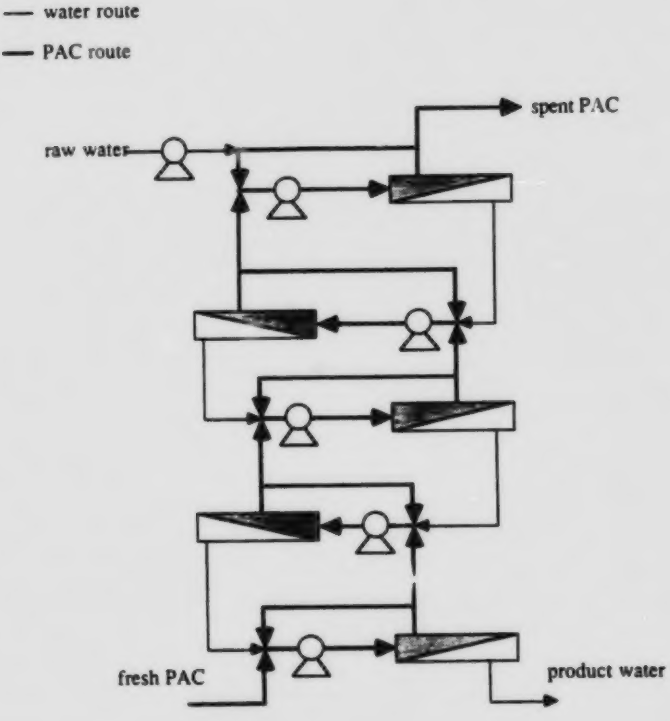
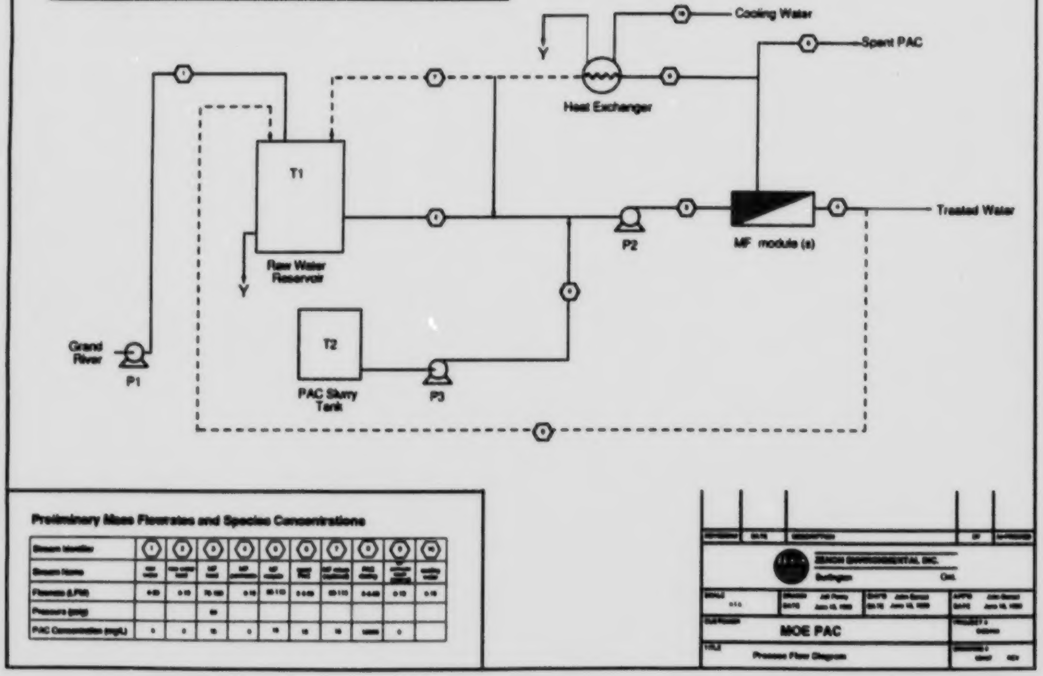

— water route
— PAC route
spent PAC
raw water
fresh PAC
product water

FIGURE 3: PAC / CFF PROCESS FLOW DIAGRAM


Cooling Water
Spent PAC
Heat Exchanger
T1
Raw Water Reservoir
Treated Water
P2
MF module (s)
Grand River
P1
T2
PAC Slurry Tank
P3
Y
ZENON ENVIRONMENTAL INC.
Burlington
Ont.
MOE PAC
Process Flow Diagram

Preliminary Mass Flowrates and Species Concentrations

Stream Identifier	1	2	3	4	5	6	7	8	9	10
Stream Name	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Flowrate (LPM)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Pressure (psig)			[illegible]							
PAC Concentration (mg/L)	0	0	[illegible]	0	[illegible]	[illegible]	[illegible]	[illegible]	0	

B15

SLOW SAND FILTRATION
PILOT PLANT TESTING OF CRITICAL QUESTIONS IN DRINKING WATER PRODUCTION

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BACKGROUND INFORMATION

In general, small remote northern communities have special conditions of climate, population, and technical expertise which must be addressed. Specifically, water treatment systems for small, remote communities should have the following important characteristics:

- Low capital and operating costs
- Simple to understand
- Minimum mechanical/electrical parts
- Low sensitivity to misuse
- Low maintenance and operating time
- Few chemical feed systems

Surface waters in the north are typically coloured and low in dissolved mineral content. Consequently, the main water treatment process objectives for these waters must provide adequate disinfection, remove colour, and control the aggressiveness of the water.

Clearly, simple processes are needed for small systems which must, nevertheless, upgrade natural water quality to drinking water standards. Most small communities could benefit from the development of simple water treatment schemes. The purpose of this study is to develop a system incorporating a simple treatment process, namely, slow sand filtration.

The overall study consists of three separate phases, as follows:

Phase I Initial Definition Program
Phase II Pilot Plant Investigation
Phase III Guidelines Manual for Design and Operation

SLOW SAND FILTRATION
PILOT PLANT TESTING OF CRITICAL QUESTIONS IN DRINKING WATER PRODUCTION

PRESENTATION OUTLINE

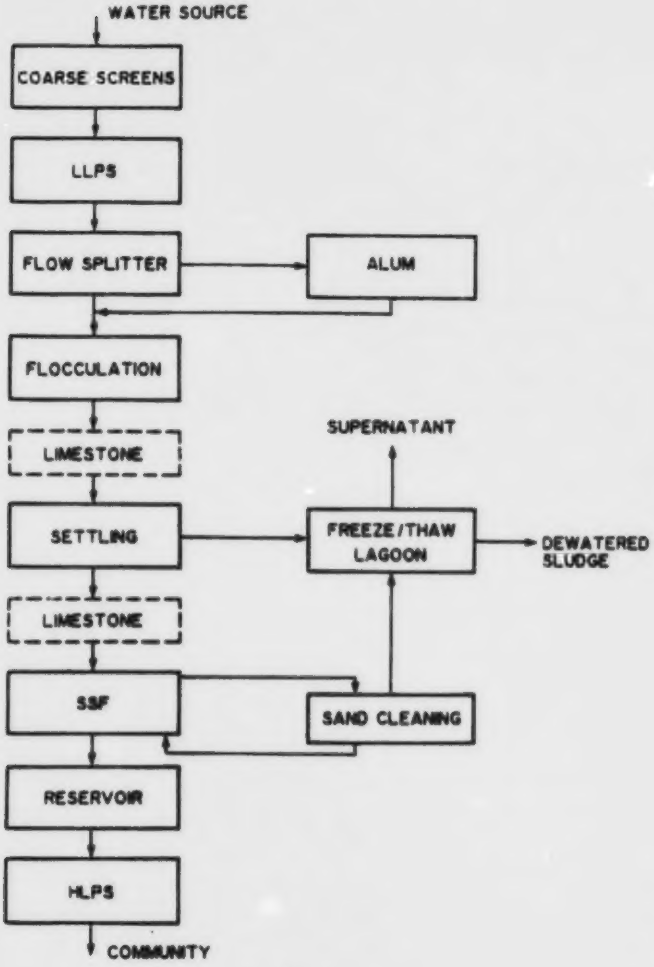
An earlier, Phase I of this project emphasized the relevant chemistry needed for reduction of soluble colour components from Northern raw water sources. This work was integrated into the slow sand filtration process for production of drinking water.

The attached diagram illustrates the type of process components which will accomplish the above water quality needs.

Phase II of this project has recently been redefined and the pilot plant work has just begun. The purpose is to answer specific questions on the placement of flocculated solids within the filter media. The results will be used in the development of models to predict filter performance. The work is ongoing at this time.

The objective of this presentation is to illustrate the direction of this project. This will be done by reviewing the earlier work, by sharing the current data from the ongoing pilot plant tests, and by detailing the phases remaining to be completed.

PROCESS FLOW DIAGRAM
POSSIBLE SLOW SAND FILTER PLANT


WATER SOURCE
COARSE SCREENS
LLPS
FLOW SPLITTER
ALUM
FLOCCULATION
LIMESTONE
SUPERNATANT
SETTLING
FREEZE/THAW LAGOON
DEWATERED SLUDGE
LIMESTONE
SSF
SAND CLEANING
RESERVOIR
HLPS
COMMUNITY

B16

EMERGING ADVANCED TECHNOLOGY FOR DESTRUCTION OF WATERBORNE ORGANIC POLLUTANTS

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INTRODUCTION

Among other water purification processes, the EPA considers only air stripping (for removal of volatile contaminants) and carbon adsorption (for removal of volatile and non-volatile contaminants) as effective treatment technologies. However, a grave weakness of air stripping and carbon adsorption is that these are non-destructive technologies. While air stripping converts a liquid contamination problem into an air pollution problem, carbon adsorption filters the contaminants and produces a hazardous waste solid which must then be disposed of. Moreover, both technologies are coming under increasing regulatory restrictions. Obviously, a destructive technology, which converts the harmful organic pollutants into totally harmless products, is required.

In 1976, Carey et al(1) of the Canada Centre for Inland Waters published a pioneering paper in which they demonstrated that pollutants such as polychlorinated biphenyls (PCB's) could be totally mineralised to CO_2*,* H_2O *and chloride ions by photolyzing* TiO_2 *(Anatase) suspensions using 365 nm UV light. Since then many others (2-11) have confirmed their initial discovery and have shown that the* TiO_2 *photocatalytic process is applicable to the photodegradation of a wide variety of organic pollutants in water systems. However, no attempt was made, over the past ten years to commercialize this process.*

Nulite, with the financial support of both the National Research Council of Canada and the Ontario Ministry of the Environment, is currently conducting intensive research to advance this photocatalytic process into a commercially viable technology for water treatment. Prototype reactors fabricated by Nulite are being tested at various academic and industrial laboratories. Various experimental parameters are being investigated by Nulite to optimize the performance of these reactors. Some results of our ongoing intensive research are discussed.

EXPERIMENTAL

The Nulite Prototype Photoreactor

The Nulite prototype photoreactor comprises a jacket, a lamp and a photocatalytic sleeve. The lamp emits ultraviolet light in the 300–400 nm range and is mounted coaxially within the jacket. Around the lamp lies a sleeve formed of fibreglass mesh which is coated with a firmly bonded layer of titanium dioxide (Anatase).

The Anatase layer is activated by ultraviolet light. Contaminated water flows through the reactor in parallel with the lamp. As the water passes through the sleeve, the open pore configuration of the mesh creates turbulent mixing. In concert with the large surface area of the mesh, this mixing ensures contact between the organic pollutants and the photocatalyst.

General Procedure

The reactor was placed vertically and connected to a 4000 ml glass reservoir and a pump. The flow of the recirculated solution through the system was controlled by changing the electrical input of the pump with a rheostat. Typically, a standard volume (3000 ml) of 10 ppm of 2,4-dichlorophenol (Kodak Chem. Co.) was prepared using organic-free water. This solution was placed in the reservoir and recirculated through the system which had been previously washed with organic-free water and drained. After a one hour recirculation of the solution at the desired flow rate, a sample was taken from the reservoir and the UV light was turned on. While the solution was recirculated through the system at a controlled flow rate, samples were then taken at regular irradiation intervals and analyzed by Gas Chromatography (GC). The GC analysis, of all samples, was performed on a Hewlett Packard 5890A instrument, using a megabore DB-5 column (30 m long, 0.53 mm diameter), an electron capture detector operating at 300 °C, and, unless *otherwise stated, direct injection of 2 µl of sample. The injection port temperature was held at 250 °C and nitrogen (14 ml/min) was used as carrier gas.*

"RESULTS AND DISCUSSION"

Photocatalytic Degradation of 2,4-Dichlorophenol

The degradation of 2,4-dichlorophenol (2,4-DCP) was chosen to test Nulite's prototype reactors for a number of reasons: (1) earlier studies suggested that complete mineralization of 2,4-DCP mediated by illuminated TiO_2 *is possible, (2) being an aromatic compound, it represents one of the main classes of environmentally important compounds for which Nulite's reactor was designed, (3) good solubility in water and low volatility allow easier sample manipulation and higher accuracy of kinetic measurements and (4) being a chlorinated compound, it can be detected with a high accuracy with the electron capture detector. The degradation of 2,4-DCP (10 ppm) in aerated aqueous solution was investigated in a continuous recirculation mode at a flow rate of 4L/min as a function of irradiation time. Figure 1 clearly shows that the reaction proceeds very efficiently, as in only 12 minutes, it was possible to bring the 2,4-DCP concentration from 10 to ~0.5 ppm. The plot of ln(Co/C) vs irradiation time (insert) shows good linearity indicating that the reaction approximates first order kinetics to a high degree of degradation (>80%). The apparent rate constant is 0.227* min^{-1} *and is found to be a flow rate dependent (see later, however).*

Effect of Flow Rate

The effect of flow rate on the degradation of 2,4-DCP (10 ppm) with irradiation time in a continuous recirculation mode is shown in Figure 2. The apparent rate constants at various flow rates and the corresponding half-life ($t_{1/2}$) *values are summarized in Table I. Clearly, the rate of degradation increases with an increase in flow rate. Apparently, this could be due to the fact that the higher flow rate maintains a higher concentration (in time) of 2,4-DCP on the* TiO_2 *surface by simutaneous replacement of the degraded 2,4-DCP molecules.*

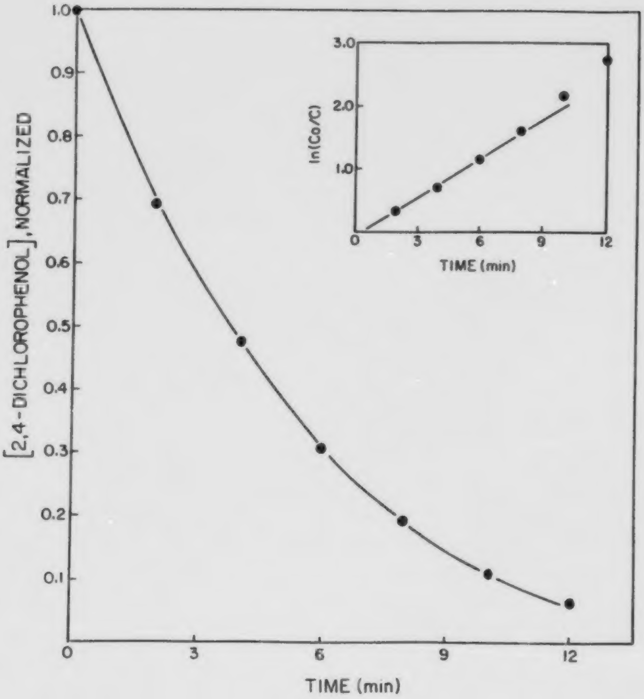

Figure 1. Plot showing the degradation of 2,4-dichlorophenol as a function of irradiation time. The insert is a plot of ln(Co/C) versus time.

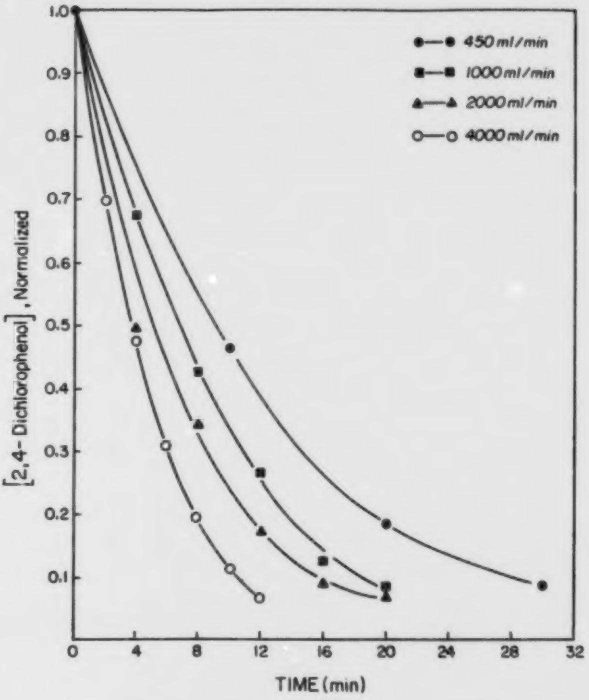

Figure 2. Effect of flow rate on the degradation of 2,4- dichlorophenol.

Table I: The apparent rate constants (k) and the corresponding half-lives ($t_{1/2}$) of the degradation of 2,4-DCP (10 ppm) at various flow rates.

Flow Rate ml/min	Apparent Rate Constant k, min^{-1}	Half-life $t_{1/2}$, min.
480	0.079	8.8
1000	0.129	5.4
2000	0.146	4.7
4000	0.227	3.1

Table II: The apparent rate constants (k) and the corresponding half-lives ($t_{1/2}$) of the degradation of various concentrations of 2,4-DCP at 3L/min flow rate[a].

[2,4-DCP] ppm	Apparent Rate Constant k,min^{-1}	Half-life $t_{1/2}$, min.
1.2	0.322	2.2
2.4	0.247	2.8
5	0.185	3.7
10	0.108	6.4
20	0.078	8.9

a) the fibreglass mesh used in these experiments is different from that in Table I experiments.

Effect of 2,4-DCP Concentration

The effect of 2,4-DCP concentration on its degradation rate was also investigated. Figure 3 illustrates the effect of the initial concentrations (1.2-20 ppm) on the photocatalytic degradation of 2,4-DCP at 3L/min flow rate. The apparent first-order rate constants k and the corresponding half-lives $t_{1/2}$ values are given in Table II.Interestingly, the k valves increase and $t_{1/2}$ valves decrease with decreasing 2,4-DCP concentration. This contradicts the first order reaction kinetics in homogeneous solutions and clearly argues in favour of surface reaction. These are important findings since the concentrations of the organic pollutants in many industrial wastes are very low (< 1 ppm).

Photocatalytic Degradation of Pentachlorophenol

Pentachlorophenol (PCP) is frequently used as wood preservative and thus it represents a very serious environmental problem. The degradation of pentachlorophenol was examined in a continuous recirculation mode with a flow rate of 4 L/min. Figure 4 illustrates the photocatalytic degradation of 300 µg (3L of 100 ppb) PCP with irradiation time. Evidently, the process is very efficient and in less than 15 minutes it was possible to reduce the concentration of PCP from 100 ppb to the recommended environmentally acceptable level of <0.5 ppb(12).

Direct Photolysis of Pentachlorophenol

The direct irradiation of 300 µg (3L of 100 ppb) PCP solution, in the absence of mesh coated with TiO_2, resulted in transformation of PCP into another product. No attempt was made to identify this product. However, the rate of disappearance of PCP via direct photolysis was slower than the photocatalytic degradation of PCP. Moreover, in the photocatalytic process (Nulite's reactor) the degradation of PCP was not associated with, this product or any other organic products for which the electron capture detector is sensitive enough. Importantly, it appears that even if this product is formed due to direct photolysis, it could not survive our photocatalytic process.

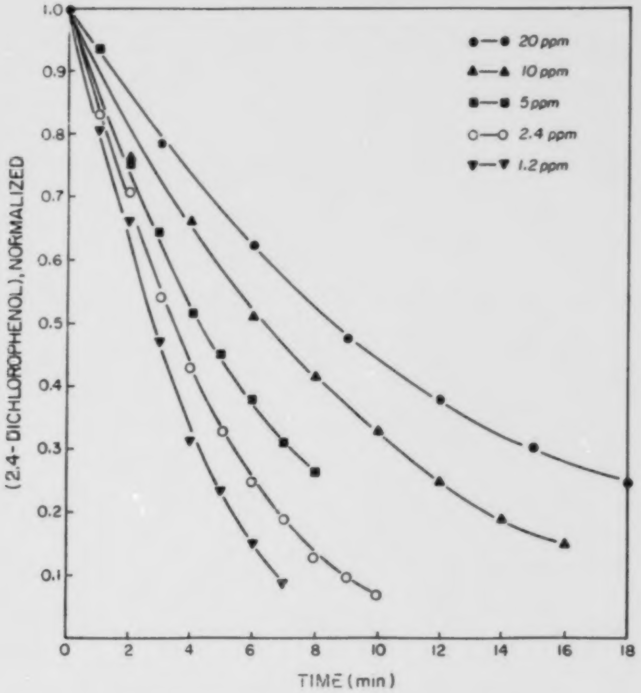

Figure 3. Effect of Concentration on the degradation of 2,4-dichlorophenol.

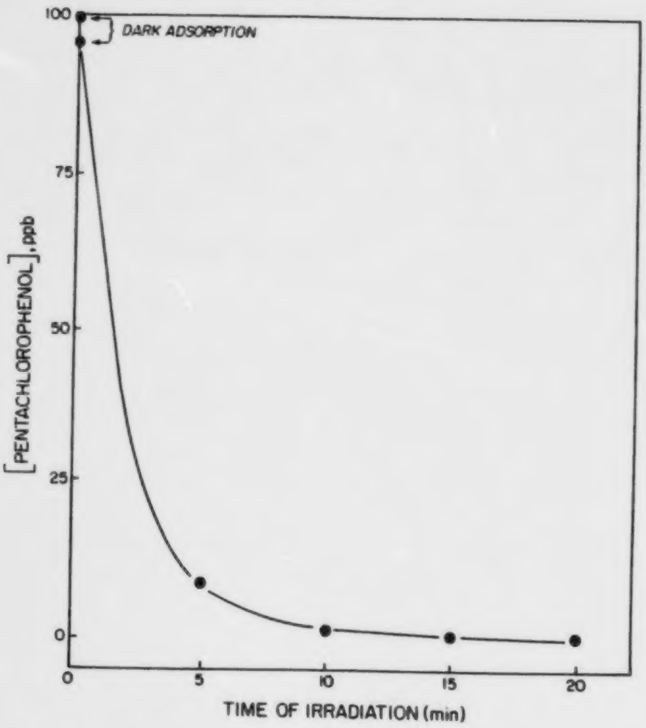

Figure 4. Plot showing the degradation of pentachlorophenol as a function of irradiation time.

CONCLUSIONS

Our previous(11) and present results clearly show that the TiO_2 photocatalytic degradation of a wide variety of organic pollutants is a highly efficient process. For example, the $t_{1/2}$ for the destruction of 30 mg of 2,4-DCP (3 litres of 10 ppm) is ~3 min. and the $t_{1/2}$ for destruction of 300 μg of PCP (3 litres at 100 ppb) is 2 min. In less than 15 min. it was possible to reduce the concentration of PCP from 100 ppb to the recommended environmentally acceptable level of <0.5 ppb. The results provide a strong promise of a clean, cheap, simple process to remove organic pollutants from natural and industrial water systems.

ACKNOWLEDGEMENT

This project has been supported by the National Research Council of Canada, Ontario Ministry of the Environment and Nutech Energy Systems Inc.

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B17

HYDROLOGIC MODEL OF DE-ICING SALTS IN THE ENVIRONMENT: A SALT BALANCE IN AN URBAN WATERSHED

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INTRODUCTION

Over the past forty years, residents of southern Ontario have come to expect bare-pavement driving conditions in urban areas and on major highways throughout the winter. As a result, tons of de-icing agents, predominantly road salt in the form of NaCl, are applied on roads. These salts accumulate in soils and in surface and subsurface waters (e.g. Diment et al., 1973; Pilon and Howard, 1987).

In response to concern for the potential environmental impact of road salting operations, a hydrologic model is being developed to predict the movement of de-icing salts and to examine the effect of repeated de-icing salt application on the quality of subsurface waters. While the paths of salt movement are understood in general terms, the relative proportion of the applied salt that i) goes directly into surface waters, ii) is flushed through the system within one year or iii) remains to accumulate in soils and groundwater, is not known. To make reasonable model predictions, an accurate measure of the amount of salt retained for each year of salt application is required for different types of watershed (e.g. urban, rural, high infiltration).

The retention rate of de-icing salts in a watershed can best be determined using a mass balance approach. For de-icing salts, the balance for a specific time period is calculated by subtracting the amount of salt (or given constituent) removed through surface water from the total input of salt (or constituent). The accuracy of the balance is determined by the accuracy of the data used. Several authors have looked at the mass balance of the chloride component of de-icing salt to understand the movement of de-icing salts and estimate the amount of salt retained in a basin or entering surface waters (e.g. Wulkowicz and Saleem, 1974; Scott, 1980; Diment et al., 1973; Paine, 1979). In these studies, calculations of the amount of salt (chloride) retained annually in soils and groundwater range from 19% to 65%. The amount retained apparently fluctuates each year. Diment et al.(1973) found that unusually high summer rainfall resulted in much higher (20%) salt removal than in the first year of a two year study. Several years of data would give the best estimate of retention, although most previous studies have only looked at a one year period. The level of detail used in previous studies to determine the inputs and outputs for the calculated balance also varied considerably. Hence, given the range of reported retention rate values and the variation in the data used, it was decided that new salt balance data should be obtained using the most accurate salt input and output data possible.

This paper addresses the development of a salt balance for the urban watershed of Highland Creek. For the first stage of this study, emphasis is being placed on the chloride component of the salt balance. The in situ monitoring instrumentation and resulting data accumulated since March, 1989, are discussed. These results provide the basis for a preliminary estimate of chloride retention in the basin and comparison with a chloride balance calculated using monthly data.

STUDY AREA

The Highland Creek basin provides a convenient location to examine the salt balance in an urban watershed and to test the in-situ monitoring equipment. The Creek flows into Lake Ontario through eastern Metropolitan Toronto. The catchment area of Highland Creek upstream of the Environment Canada weir is approximately 82 sq.km. The actual catchment boundaries were determined using storm sewer drainage areas and topographic data.

The basin is almost entirely urbanised, with recreational open space along the main Creek valley and some remaining undeveloped land in the extreme northeast. The surface sediments are predominantly silty sand till (Karrow, 1967). The basin is crossed east-west by Highway 401 (12 lanes wide), and by a grid of 2- to 4-lane arterial roads about 1.5-2 km apart. These roads and numerous secondary roads are regularly salted throughout the winter season by five agencies: the Ontario Ministry of Transportation (MTO), Metropolitan Toronto, City of Scarborough, Town of Markham and the Regional Municipality of York. It follows that this basin is characterized by high chloride inputs and high runoff coefficients.

METHODOLOGY

In Situ Monitoring

Chloride concentration fluctuates rapidly in Highland Creek during the winter period. It was thought that daily or bi-weekly sampling as used in previous studies would not give an accurate measurement of the amount of chloride discharged from the basin through the Creek. Therefore, an in situ monitoring system was developed to provide continuous or very frequent chloride data retrieval. This would detect all fluctuations in chloride concentration in the Creek and remove the necessity of daily or more frequent sampling during winter.

Because no reasonably priced, reliable and rugged chloride monitor was available, electrical conductivity was selected as the parameter to measure in the field. The measured conductivity can be converted to an equivalent chloride concentration using a relationship for the Creek developed by frequent sampling (Figures 1A,1B).

In July 1986, a YSI conductivity probe was installed in Highland Creek at the Environment Canada weir to test the equipment for continuous monitoring. Within days, the meter was damaged by a nearby lightning strike and the probe was buried in the stream bed.

In March 1989, an IC Controls conductivity probe model CC01 was installed near mid-stream at the weir. The probe is rugged in construction being designed specifically for industrial applications. The sensor and sensor electronics are sealed in a PVC housing and connected by cable to the conductivity meter in the Environment Canada monitoring station. Voltage output from the meter is recorded every 15 minutes by a Lakewood LE8200 data logger. Data are retrieved periodically from the data logger using a laptop computer. The data logger software allows an instant graphical view of collected data (Figure 2).

The probe sensors are cleaned every 3-4 weeks with a very fine abrasive. Algae that accumulates during the summer on the protective mesh around the probe tip is removed manually and appears to have no effect on the probe function.

The probe was initially calibrated and tested for drift in the laboratory using NaCl solutions of known conductivity. However, after installation in the Creek, a consistent difference was observed between conductivity values calculated from the in situ conductivity readings and values measured from stream samples. This discrepancy is largely the effect of monitoring in a flowing stream versus calibrating in 'still' solutions. The conductivity probe is now calibrated by measuring the stream conductivity in the field using a portable conductivity meter and using this value to set the meter.

Chloride/Conductivity Relationship

The relationship between conductivity and chloride concentration in Highland Creek is required to convert the in situ monitoring data to an equivalent chloride concentration for use in calculating the chloride balance. This relationship is determined using numerous Creek samples taken through the year. Samples are analysed in the laboratory for chloride and conductivity using an Orion combination chloride electrode and a YSI conductivity meter respectively. These data and the monthly MOE chloride data for Highland Creek are used to develop a chloride/conductivity relationship for the Creek waters, as illustrated by Figures 1A and 1B.

The chloride and conductivity data obtained by the field sampling are used also to cross-check the in situ monitoring data.

CHLORIDE BALANCE CALCULATION

The watershed chloride balance is calculated by determining total chloride input to the catchment and subtracting the chloride leaving the watershed by surface water. The difference represents the amount of chloride retained in surface waters, soils, and subsurface waters. In this study, the amount of chloride leaving the basin through stream sediment load is assumed to be negligible.

Chloride Input Data

Road salt is the major source of chloride entering the basin. It is applied as pure salt (NaCl) or as a salt/sand mixture. Total salt application in the study area during the winter of 1988/89 was 18100 Mg or metric tonnes (Figure 3C). Total chloride input from road salt and other sources is estimated at 11600 Mg (+/-5%) for 1988/89.

Daily salt application was determined from the yard records of the five agencies applying salt. The proportion of each salt/sanding route within the basin was multiplied by the amount of salt applied on the route. It was assumed that salt was applied evenly along a specific route. To estimate the amount of salt applied to parking lots, the rate of salt application was assumed to be the same as the rate for major roads for shopping centre lots and one-half this rate for other lots (Scott, 1980b). Salt on parking lots represented about 14% of the total salt applied. Application by private home-owners was estimated by multiplying the approximate number of single-family residences by an average annual rate of 4 kg/household. This represented less than 1% of the total salt application.

Other sources of chloride are relatively insignificant. Chloride concentration in precipitation around Metropolitan Toronto during 1986 averaged 0.2 mg/l (Ontario Ministry of the Environment 1988), which converts to approximately .1% of the total chloride inputs. A calcium chloride de-icing additive used occasionally in the area represents less than 0.1% of the input. There are no known sanitary-storm sewer interconnections in the basin (Scarborough Works; per. comm.). Depending on the chemical formulation, fertilizers may contain a significant amount of chloride (Hunter and Associates, 1987). However, the potential contribution from fertilizers has not been quantified at this time.

Chloride Output Data

Chloride discharge or "loading" in a stream can be calculated by:

$$Cl = Cm \times Q$$

where Cm is mass concentration and Q is stream discharge. Cl represents the total chloride "loading" and includes chloride contributions made from groundwater to the stream during base flow. In order to consider the amount of chloride retained in the basin as a result of a single winter's salting, the total loading was corrected for the contribution to the chloride load coming from previous chloride accumulation in the watershed. This contribution or base load was calculated using a chloride concentration (Cb) of 100 mg/l and a base level discharge (Q) of 0.5 cu.m/sec. This preliminary estimate of base load will be revised after the 1989 monitoring is complete,when data are available for the chloride concentration in the Creek immediately before the next winter salting starts.

Chloride discharge is calculated from the in situ monitoring data by converting the conductivity values, corrected for the flow effect, to chloride concentration using the appropriate chloride/concentration relationship (Figure 1). Concentrations are then multiplied by the corresponding stream discharge (also measured at 15 min. intervals) to give the chloride load or discharge in the Creek, and then corrected for base load. Figure 4A and 4B illustrate chloride discharge and chloride concentrations in Highland Creek between March 10 and April 27, 1989.

Because a full year of data is not yet available from the in situ monitoring, an estimate of annual chloride discharge was made for a 12 month period (June 1988 - May 1989) using MOE monthly chloride data supplemented with chloride data from this study, and the average daily stream discharge (Figure 3A).

RESULTS AND DISCUSSION

In Situ Monitoring

Detailed chloride discharge data have been obtained for Highland Creek from March 10, 1989 to the present. The instrumentation has proved relatively reliable. A gap in the data for May was caused by damage due to vandalism. Some minor gaps also occur during the summer as a result of a power failure and an electrical short. However, interpolations can be made readily using the existing data base.

Figures 4A and 4B present the in-situ chloride data for March 10 to April 27, 1989. The rapid changes in chloride concentration and chloride mass discharge are clearly visible during mid-March.

These rapid fluctuations occur in response to salting during this time (Figure 4D) and can be correlated with salt application, precipitation, and increased stream discharge.

The summer data are not presented here; in summary, since late April, chloride concentrations during periods of base stream flow have declined from approximately 300 mg/l to 150 - 100 mg/l in early fall. Lower concentrations, but not lower mass discharge, are associated with high stream flow following rain. The general pattern of chloride discharge is similar to the summer portion of Figure 3A, with rain flushing some of the retained winter salt into the surface water. There is also a diurnal fluctuation in conductivity and chloride concentration of approximately 10%. More detailed analyses are in progress to characterize this pattern and determine if it has any significance.

Daily chloride discharge calculated using the in situ monitoring data (discharge and chloride) and the daily samples with daily average discharge were compared for the March - April period. Overall, the daily values gave only a 3% higher chloride discharge than the in situ monitoring. Differences were greater on specific days. For example, on March 22 chloride concentration fell as the effect of salt-laden runoff from the previous days salt application declined. The chloride measurement was taken early in the day. An afternoon increase in runoff due to snowmelt increased the flow but not the chloride concentration to the same extent. Therefore, the daily chloride discharge incorporated the increased flow but not the fluctuation in chloride, resulting in a 19% overestimate above the chloride discharge calculated using the in situ monitoring data. Differences in the calculated chloride discharges using in situ monitoring versus daily sampling are expected to be greatest during the winter salting season when daily sampling can readily miss major runoff events and when chloride concentrations fluctuate rapidly. (See Figure 4B.)

Comparison of a full year's data from the in situ monitoring and daily sampling will be required to determine if the two methods yield equivalent results over a year or a season. While the in situ monitoring provides much more detailed data and is useful for analysing very specific events, the probe must be regularly maintained, calibration checked and the stream sampled to check results. Although the in situ monitoring reduces travelling time for sampling, data gaps that occur due to power failure, or malfunction are not detected until the next site visit; also, time is spent simply processing the large volume of generated data.

Chloride Balance

The detailed chloride discharge for March 10 to April 27 is given in Figure 4A. The net balance during this time is 200 Mg chloride retained in the watershed, or about 9% of inputs for this period. This relatively low retention is expected for spring runoff in an urban basin. The high chloride discharge on March 14 is caused by rain and above freezing temperatures which would have removed snow and some previously applied salt, as well as salt applied that day, from the ground surface. On this date, both stream discharge and chloride concentration increased. By late March and into April, (Reading 2350, 3200,3300,and 4150 on Figure 4B), high stream discharges cause a lowering or diluting of the chloride concentration although the mass of chloride discharged from the stream is increased (Figure 4A). By the end of April, repeated rain and complete snowmelt will have flushed winter salt from the surface. Rain during the summer season continues to flush salt through the upper soil profile and in to the groundwater.

Close examination of the period from March 17 to 22 provides details on chloride balances for specific storm events and on the occurrence of chloride-laden runoff. On Figure 4A there are two similar large chloride discharges - on March 19 and on March 22. The first occurs after heavy salting on March 17 and 18 for freezing rain and snow. In the period of March 17 to 19, about 48 % of the chloride applied is removed, mostly on the third day. On March 20, more snow fell and salt was applied on the 20th and 21st. In this case the chloride discharge peaked on the 21st during continued salting operations. An amount equivalent to 67% of the chloride applied during this period was discharged to the Creek from March 20 to 22. Some of this chloride would have been applied in the earlier period. The difficulty in predicting when major chloride discharge may occur and in determining the proportion attributable to specific inputs, underlines the need for detailed monitoring and sequential balances.

An overall salt balance cannot be determined from the in situ results until a full year's data are collected. However, since the chloride discharge of March 10 to April 27 includes chloride from salt applied prior to the spring period and the flushing of any salt remaining on the road surface, the 9% retention rate represents a minimum for this period. It follows that this figure indicates that a minimum of 9% salt was retained in the watershed for the 1988/89 winter.

An annual salt balance was calculated for the period June 1988 to May 1989 using the monthly MOE chloride data for Highland Creek. While this balance gave a net loss of chloride from the basin of approximately 14%, this figure is known to be incorrect. This occurs because the balance was calculated assuming that a single chloride concentration could be applied to all discharges for a given month. Unfortunately the December chloride concentration of 2850 mg/l was obtained on the first clear day after eight days of salt application (3310 Mg) when chloride concentrations were temporarily extremely high. This results in a huge chloride discharge (50% of the total) being calculated for December (Figure 3A). However, this balance is useful for showing general patterns of chloride discharge through the year and for emphasizing the need for frequent data collection when calculating the chloride mass discharge.

The chloride balance determined for Highland Creek using the in situ data should be characteristic of urban areas in southern Ontario. Using a entire catchment, rather than a specific site, smooths out some of the local effects of slope, surface condition, spread of spray from vehicles at different speeds, and variations in salt application rates. Therefore, the chloride balance and estimated retention rates should be suitable for characterizing urban areas within watersheds in the hydrologic model.

CONCLUSIONS

1. Chloride is being retained in the Highland Creek basin. The actual salt balance and determination of retention time requires a full years' data, and preferably several sequential years of data. This balance should be representative of urban areas throughout southern Ontario for modelling purposes.

2. The in situ monitoring data and daily stream sampling gave similar salt balance results for the March - April period. The in situ monitoring provides more detailed data and requires less manpower time, especially if a site is more remote. However, some sampling is still necessary to maintain calibration and certify results. A full year of testing is required to fully assess the reliability of the in situ equipment and to determine wether better data are obtained.

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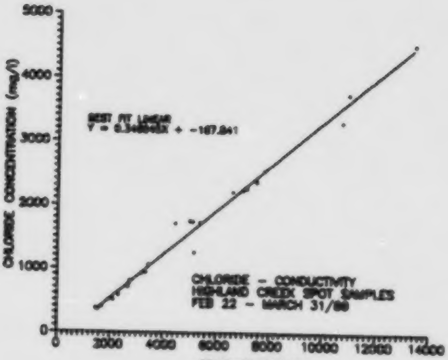


FIGURE 1A: MARCH CHLORIDE/CONDUCTIVITY RELATION

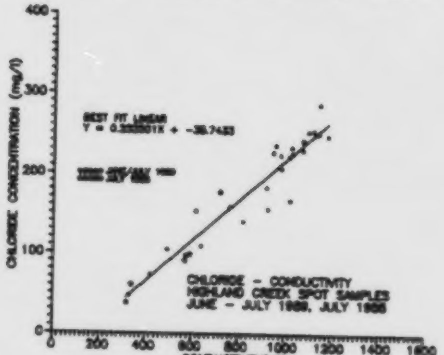
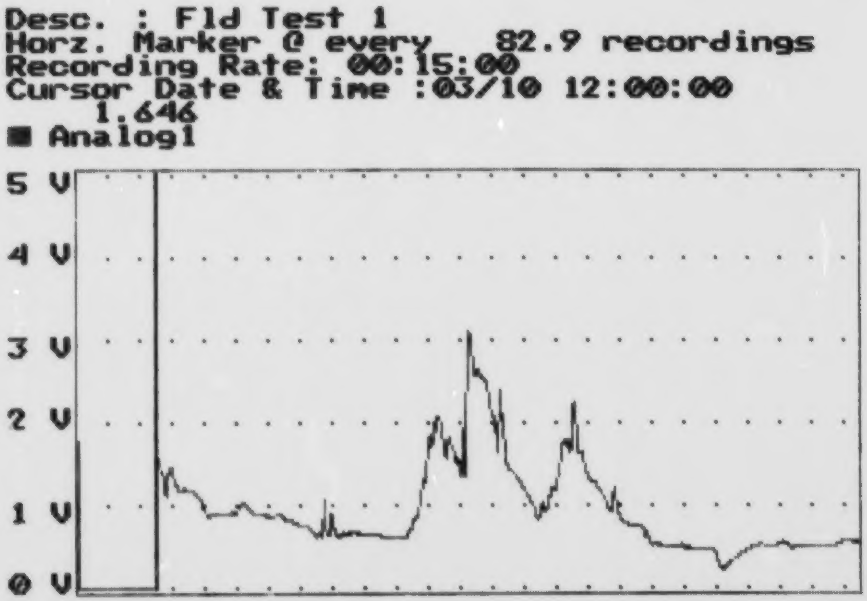


FIGURE 1B: JUNE/JULY CHLORIDE/CONDUCTIVITY RELATION



Desc. : Fld Test 1
Horz. Marker @ every 82.9 recordings
Recording Rate: 00:15:00
Cursor Date & Time :03/10 12:00:00
1.646
■ Analog1

Note: 3 volts = 10000uS
FIGURE 2: DATA LOGGER FILE, HIGHLAND CREEK CONDUCTIVITY READINGS, MARCH 10 TO MARCH 29

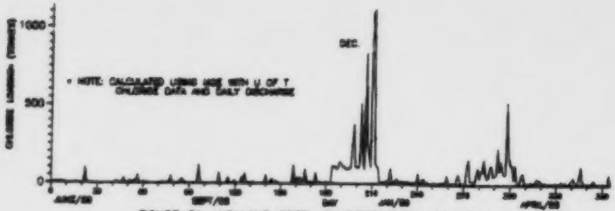


FIGURE 3A: HIGHLAND CREEK CHLORIDE DISCHARGE* 1988 – 1989

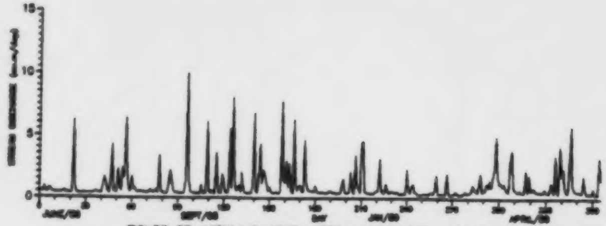


FIGURE 3B: HIGHLAND CREEK STREAM DISCHARGE JUNE,1988 – MAY, 1989

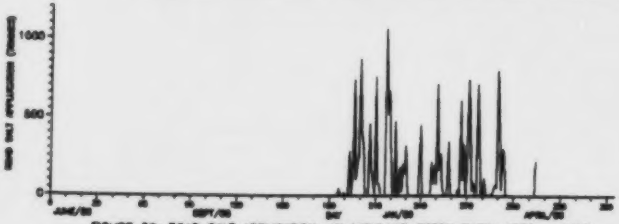


FIGURE 3C: ROAD SALT APPLICATION IN HIGHLAND CREEK BASIN 1988 – 1989

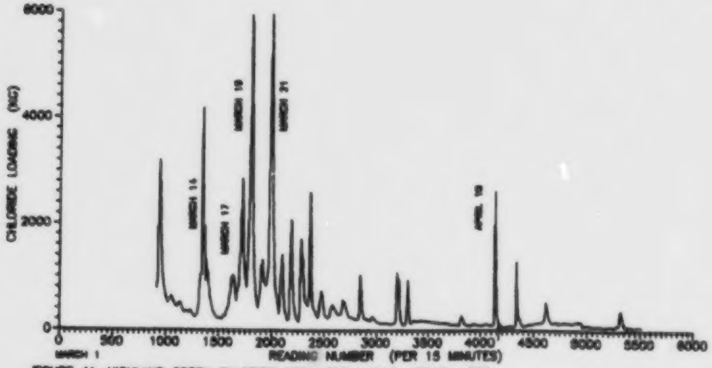


FIGURE 4A: HIGHLAND CREEK CHLORIDE DISCHARGE MAR.10–APR.27, 1989

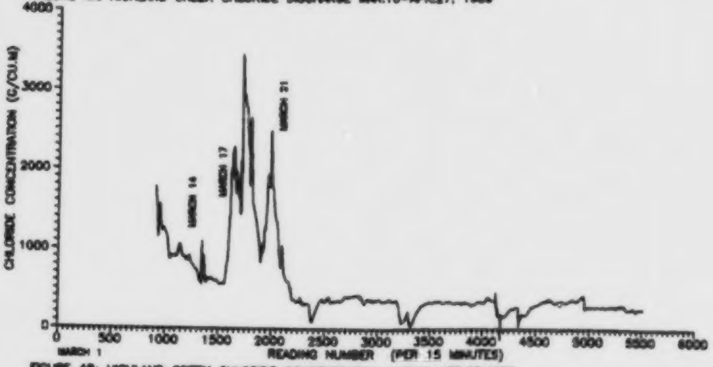


FIGURE 4B: HIGHLAND CREEK CHLORIDE CONCENTRATION MAR.10–APR.27,1989

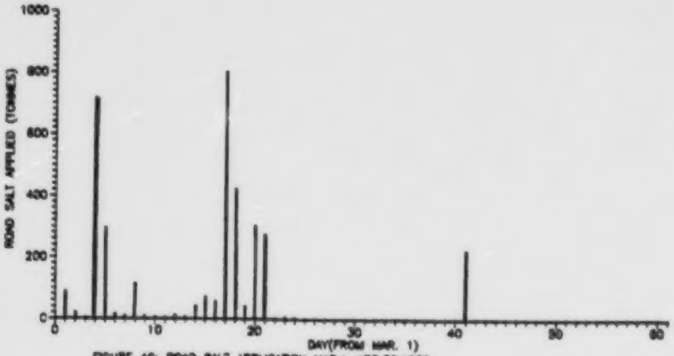


FIGURE 4C: ROAD SALT APPLICATION MAR.1–APR.30,1988

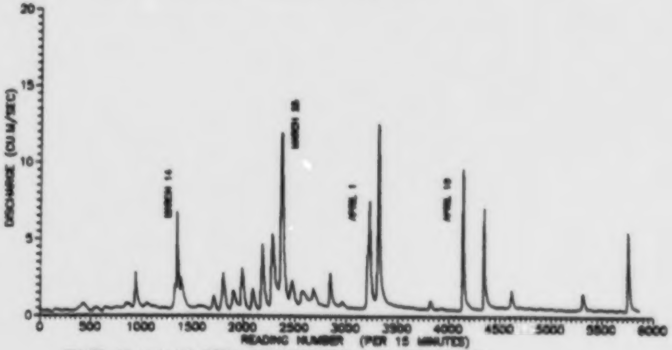


FIGURE 4D: HIGHLAND CREEK DISCHARGE MARCH 1 TO APRIL 30,1988

B18

Test of a Chemical Mechanical Process for the Decontamination of Non-anatomical Biomedical Waste

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INTRODUCTION

The amount of solid waste generated by hospitals has been increasing every year. Infectious waste management presents many problems for health care facilities. Steam sterilization and incineration are most commonly used for waste treatment; however, each method has significant disadvantages. An alternative mechanical/chemical infectious waste treatment process has been developed that grinds the waste to a granular size and simultaneously treats it with a 12% sodium hypochlorite solution. Although some work has been done to assess the efficiency of this novel biomedical waste treatment system (Denys, 1989), more extensive studies are required.

Aqueous chlorine, generally accepted as a universal water disinfectant, is a potent bacteriocide under optimal conditions. The stability of free chlorine in solution depends upon many interacting factors. In general, (1) a decrease in pH results in a corresponding increase in bactericidal activity, (2) an increase in temperature increases antimicrobial action, and (3) an increase in chlorine concentration increases killing ability. Microorganisms that are associated with particulate matter may be protected from contact with the chlorine and remain viable.

The objectives of this study were to determine the effectiveness and limitations of chlorination for the inactivation of bacteria and viruses in infectious hospital wastes.

METHODS

Test Organisms

The basic requirements of indicator organisms are that they should be present whenever pathogenic organisms are present, they should be resistant to treatment processes, and they should be detectable by practical techniques. *Bacillus subtilis*, *Mycobacterium smegmatis*, *Serratia marcescens* and *Escherichia coli* phage T4rII were chosen for study because they possess the aforementioned characteristics.

The test organisms were used to evaluate the disinfecting efficacy of free available chlorine incorporating the following experimental parameters:

1) hypochlorite concentration;
2) pH; and
3) chlorine - cell contact time.

To assess the effect of adsorption of organisms to solids coliphage and *S. marcescens* were mixed with sterile shredded hospital waste prior to chlorine treatment.

RESULTS

The organisms were exposed to different chlorine concentrations at a pH of 4,5, 9 and 10 for varying periods of time. The conditions required to produce complete kill of the test organisms are described in Table 1.

Table 1: Time and Chlorine Concentration Required to Produce 100% Inhibition at Various pH's

Organism	pH	Free Chlorine (ppm)	Time (min)
B. subtilis	4	300	120
	5	100	60
	9	10	60
	10	0.3	120
M. smegmatis	4	0.3	30
	5	100	30
	9	100	60
	10	30	120
S. marcescens	4	3000	30
	5	1.0	60
	9	10	120
	10	0.3	120
E. coli T4rII	7	0.1	1

The relationship between adsorption of cells to inanimate hospital waste and inactivation by hypochlorite was also investigated. It was found that within 10 to 15 min 4% of the *S. marcescens* cells and 7% of the *E. coli* T4rII phage had adsorbed onto the inorganic surfaces. An additional 30 min contact time between the chlorine and the adsorbed cells was required to obtain the same degree of inactivation of *S. marcescens* at a given hypochlorite concentration.

DISCUSSION

Analysis of the efficacy of chlorine disinfection was studied using relatively resistant, fastidious strains of bacteria as test indicators. The coliphage *E. coli* T4rII was found to be very sensitive to chlorine. Future studies will include coliphages, such as the f2 bacteriophage (Keswick *et al.*, 1985), that are known to be chlorine resistant.

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VOLUME I
SESSION B
WATER QUALITY RESEARCH
POSTER PRESENTATIONS

BP1

Assessment of Contaminant Migration from Industrial and Landfill Sources in the Twelve-Mile Creek and Welland River Watersheds and their Impact as Inplace Pollutants in Sediments

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Analysis of sediments from Twelve-Mile Creek for organic contaminants, and analysis of sediments from the Welland River for organic and inorganic contaminants have been performed. Results show little contamination of sediments in both locations by organic compounds. Inorganic contamination of the Welland River in the vicinity of Atlas Steels is more severe.

Analyses for chromium, copper, iron, lead, nickel, and zinc have been performed on sediments upstream and downstream from the city of Welland. These sediments reveal that concentrations of heavy metals in sediments of the south side of the river increase dramatically in the vicinity of the Atlas Steels outfall. Contamination of the sediments remains high for some distance downstream from the outfall and, as the river bends, the sediments on the north side of the river start to show elevated levels of heavy metals. Since the flow regime in the Welland River is quite complex, due to varying demands on the hydro-electric power canal, some distance downstream from the Atlas Steels plant, it is possible that there are times when the flow of water along the river is halted. The introduction of contaminants into the river during these slack water events may account for the appearance of contamination some 60 metres upstream from the Atlas outfall.

We have performed a sequential extraction procedure, based on the method of Tessier, which provides a measure of the availability of metallic ions bound to sediments. It is clear that significan amounts of heavy metals are readily available to the aqueous environment. Levels of nickel in neutral extracts of the sediments are sufficiently high to be a cause of concern. It has been reported that nickel at concentration of 5 ng ml^{-1} may be responsible for the extermination of ***Dapnia*** species in the Don River in the USSR.

Our studies of the sediments in the Twelve-Mile Creek and the Welland River have failed to show any substantial concentrations of PCBs. The recent reports of PCBs in snapping turtles from Twelve-Mile Creek is not reflected in our findings in fish. Unusual aromatic hydrocarbons (for example, hexaethyl benzene) appear in the sediments at the junction of the first Welland Canal and Twelve-Mile Creek. These compounds may derive from transformer oils. In addition, complex mixtures derived from paper making operations in Thorold were identified.

During the course of this work, we have developed some modifications to the way in which analyses are performed with the Hewlett-Packard 5890 system using splitless injection. Thus we have been able to achieve a 20-fold increase in signal from late eluting PAHs in the GC/MSD system. We have found that the use of dichloromethane and isooctane, both popular solvents for the introduction of samples into the GC are inferior to p-xylene. Important modifications to the temperature programme must be made in order to achieve the improvement in sensitivity that is reported here.

We have used the improved sensitivity to investigate the occurrence of PAHs in the Welland River. These results will be reported at a later date.

BP2

THE USE OF *TRADESCANTIA* AND *VICIA FABA* BIOASSAYS FOR THE *IN SITU* DETECTION OF MUTAGENS IN AN AQUATIC ENVIRONMENT.

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Tests have shown plant bioassays to be excellent for mutagenicity studies. Most studies, however, have been carried out in the laboratory, or if *in situ* as monitors of atmospheric contaminants. The primary purpose of this study was to assess the utility of *in situ* plant mutagenicity bioassays in monitoring water contaminants. The assay systems tested were the *Tradescantia* stamen hair and micronucleus assays for the detection of gene mutations and chromosomal aberrations, respectively, and the *Vicia faba* root-tip bioassay which detects chromosomal aberrations. The assays were used to test the effluent from a pulp and paper mill located on the north shore of Lake Superior. Assays were performed in a creek containing raw effluent and in a bay of Lake Superior into which the creek emptied. In the creek, 11.5 km from the source, the effluent was toxic to the *Vicia faba* roots as evidenced by a reduction in the mitotic index. The effluent in the creek induced a significant increase in the number of stamen hair mutants, micronuclei, and chromosome aberrations. In that section of the bay clearly contaminated by the creek effluent, we also measured increases in mutagenicity. *Tradescantia* assays performed in the laboratory several days later with water from the test sites, demonstrated decreased mutagenicity compared to the *in situ* tests. If this proves to be a general phenomenon, testing aquatic environments should be done *in situ* or as soon after water sampling as possible. Our data demonstrate that these plant assays are sensitive and effective monitors of water quality when used *in situ*.

BP3

LANDSAT-5 TM SPECTRAL RESPONSES FOR LAKES ACROSS NORTHERN ONTARIO

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Over the past two years we have reported on the progress of M.O.E.-funded research initiated to investigate the feasibility of using satellite remotely sensed data for the determination of surface water quality characteristics of inland lakes in Ontario. Within Northeastern Ontario several water parameters (especially Secchi disc depth and dissolved organic carbon) were capable of being predicted with considerable confidence by employing multiple regression models (Pitblado 1987; Pitblado et al. 1987). The use of an image analysis maximum likelihood classifier enabled us to discriminate between acidic and non-acidic lakes in a relatively small area north of Lake Wanapitei (Pitblado 1987, 1988).

Further contributions in this field require a more thorough understanding of the multivariate structure of the Landsat-5 Thematic Mapper (TM) scanner responses from lakes throughout the Canadian Shield. Toward that end, we began to highlight the various spectral responses associated with Northeastern Ontario lakes with differing concentrations of DOC (Pitblado and Dempsey 1988, 1989). The latter efforts were based on the principal components analyses (PCA) of the seven TM channels, within and between selected DOC concentrations and the suggestion that other water parameters might also serve to bring out the structure of TM spectral responses.

In this poster presentation, these analyses are extended to a set of 346 lakes in Northwestern Ontario and compared with the earlier results from the Northeast which were based on a set of 633 lakes. The eastern study area covers almost all of Northeastern Ontario from Highway 11 (Hearst to Cochrane) south to the North Channel of Georgian Bay; the Northwest study area is much smaller, focused on Quetico Provincial Park but extending a little north of Atikokan and also east towards Thunder Bay. In addition to PCA, we have employed several other multivariate analysis techniques (cluster and discriminant analyses) as all three have consistently aided us over the years in bringing out comparisons and contrasts in abiotic and biotic parameters for lakes with varying trophic characteristics (e.g. Pitblado et al. 1980; Keller and Pitblado 1989).

The surface water quality data available for these analyses, collected either by ourselves or through access to databases of the Ontario Ministries of the Environment and Natural Resources, are almost identical with respect to the parameters that would enable comparisons between the Northeast and the Northwest. Table 1 in the poster display summarizes some of the statistical features of the 22 variables common to both data sets. Note that for each region between 5 to 10 percent of the study lakes (i.e. those examined using TM digital data) have corresponding water chemistry data.

A key observation to be made in reviewing Table 1 is the conspicuous (for us) absence of the two most important, optically relevant parameters which we have been using to assess the relationships between satellite scanner responses and lake water quality: Secchi depth and dissolved organic carbon! While these variables are contained in the Northeastern data sets, they were not available to us for the Northwestern. The optically significant parameter common to the two data sets was apparent colour measured in Hazen Units. While this diminished the number of study lakes with field data, it was found useful for the present comparisons. (Note: for Northeastern lakes the correlation coefficients between dissolved organic carbon and apparent colour range from 0.67 to 0.98, depending on the selected subsets of lakes chosen for analysis; overall, $r = 0.78$, $P < 0.001$, $n = 92$).

As with our work with DOC (Pitblado and Dempsey 1988, 1989), we subdivided our study lakes into four categories based on the following ranges of apparent colour: < 10, 10-20, 20-30, and > 30 H.U. When not subdivided into these groups, the eigenstructure of the TM data based on all mean pixel values shows that the major variance in reflectance for lakes can be attributed to the TM channels in the visible portion of the electromagnetic spectrum; with lesser proportions explained by the near-infrared then thermal channels. The first three principal components account for 84.3% of the variance for the Northwestern study lakes and 91.4% for the Northeastern study lakes. The visible-then-infrared sequence of components are in direct contrast to many published works on the applications of PCA in remote sensing. The normal expectation would be for an infrared-then-visible series of components because such work has focused on terrestrial targets. There the great variety of vegetation types results in a PCA-1 that discriminates between the high infrared reflecting targets of forest and crop land to the low infrared reflecting surfaces of plowed fields, cutovers, or lands in rural-to-urban conversion.

When the apparent colour groups are employed, the low colour lakes are discriminated primarily by the near-infrared channels rather than the visible. This may seem paradoxical, as we have argued (Pitblado and Dempsey 1988, 1989) that the addition of TM1 (blue) to the Thematic Mapper is one of the strengths of that scanner for water quality analyses compared to the band selections available for the Landsat MSS or the SPOT HRV instruments. It would appear that it acts as a controlling variable, in the sense of a partial correlation, when all water bodies are being examined. TM1 plays a much more significant role when contrasting water bodies of higher colour. The principal components pattern of infrared-visible for low colour lakes then visible-infrared for high colour lakes applies, with minor variations, to both Northwestern and Northeastern lakes. A significant difference occurs with the thermal channel (TM6) where, in association with the very clear acidic lakes in the east, TM6 is negatively correlated with components in the Northeast but positively correlated in the Northwest.

These same categories of apparent colour were employed to discriminate our study lakes on the basis of either TM reflectance values or field-collected water quality parameters. Simply on the basis of these colour categories, correctly classified percentages (multivariate discriminant analysis) ranged from 85% to 100% using field data, with the variations depending on the subsets of lakes employed in the analyses (i.e. contrasts between the Northwest and the Northeast or subsets within each of the two major study locations). The identical colour categories yielded percentages from 66% to 100% for the discriminations based on TM reflectance variables.

Our final sets of analyses were based on the use of numerical taxonomy (cluster analysis) where, for each of the two regions, the lakes were classed on the basis of untransformed TM spectral responses. The spectrally defined groups were then used to see whether they could be discriminated solely on the basis of water quality parameters that had been determined by field and lab investigations. Multivariate discriminant analyses yielded correct classification percentages from 65% to 100% (mostly in the 85% to 95% range), again depending on the lake subsets employed in the analyses.

Reasonable explanations can be found for the high order of classification accuracies based on the TM reflectance channels within the apparent colour categories. After all, the remotely sensed data is looking at differences in "colour". At this point in time, however, we do not yet have full explanations for the similarly high classification accuracies associated with water quality parameters within the clusters defined by TM channels alone. These are astonishingly high percentages given the dearth of water parameters that would be considered to be optically significant. Our poster highlights the areas and lakes where discriminations were either successful or not.

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BP4

THE ORIGIN AND DISTRIBUTION OF METHANE IN THE ALLISTON AQUIFER COMPLEX ,SOUTHERN ONTARIO.

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Methane (CH_4) is a major groundwater contaminant in some parts of the Alliston aquifer complex. This aquifer is a major water resource for present and future population growth over an extensive region, including Alliston, Newmarket and Cookstown. The goal of this research is to establish the distribution pattern of CH_4, and to provide a reasonable model for the origin and prediction of CH_4 in the aquifer.

The presence of methane in groundwater could be a result of in situ production by bacteria (methanogenesis); this type of methane is referred as "biogenic methane". Another source is migration of gases from bedrock reservoirs. In general, this last type is formed by thermal degradation of organic matter during burial and diagenesis and is called "thermocatalytic".

Two hypotheses may explain the occurrence of methane in the Alliston aquifer. One suggests the occurrence of methane is controlled by the nature of the underlying Paleozoic bedrock. Where the bedrock is shaley (Collingwood, Blue Mountain Groups), insignificant amounts of gas are found. However, where the bedrock is limestone (Trenton Group), methane is found at high concentrations. This implies that the source of methane is leakage or migration from the more permeable limestone bedrock. This hypothesis is encouraged by the fact that methane is likely present in the Trenton Group. It is well documented that these carbonate rocks are an important reservoir for natural gases in other part of southern Ontario.

The second hypothesis, based on carbon isotope analyses of methane from some overburden wells, suggests the methane is biogenic in origin, produced by bacterial action. This implies that methane is produced within the aquifer, since methane found in the Trenton rocks has a different isotopic composition, typical of thermocalytic methane. Therefore, bedrock control of the occurrence of methane appears to be unlikely.

The research approach includes the use of geological, hydrological and geochemical tools. The main geological aspect that has been investigated is the nature of bedrock lithology. A topographic and lithological map for the bedrock have been constructed. This map and information regarding the distribution of methane in the aquifer have been used to test the hypothesis of bedrock control on the presence of methane in the Alliston aquifer. A map of the regional groundwater flow pattern has been updated to analyze the possibility that methane could be produced in specific areas of the aquifer and transported as dissolved constituent by groundwater to others part of the aquifer.

An extensive groundwater sampling program that includes deep overburden and bedrock wells, representing most of the aquifer, has been carried out in order to evaluate the distribution of methane and geochemistry of groundwater in the aquifer. Sampling included gas collection for chemical and isotopic analyses, with emphasis on methane concentration and ^{13}C, ^{14}C and ^{2}H isotopic composition. These tracers provide information about the origin of the methane. Water samples were collected for chemical and isotopic analyses, including ^{18}O, ^{2}H in water and ^{14}C and ^{13}C in dissolved inorganic carbon

(DIC). These isotopes provide information about the origin and residence times of the groundwater. Dissolved organic carbon (DOC) samples were collected for concentration and ^{14}C, ^{13}C analyses. These provide information about the potential carbon sources for methane. Gas analyses also include hydrocarbon molecules heavier than the methane (C_2 to C_4). The presence of these molecules are an indication that the methane is thermocatalitic in origin.

The main components of gas extracted from the groundwater are CH_4 and N_2. These two compounds comprise about 80 o/oo and 20 o/o of the gas respectively. However, in some groundwater the opposite composition is observed. Effort will be made to explain the origin of the nitrogen in the groundwater. No traces of C_2 to C_4 hydrocarbon molecules have been found in the gas samples.

The major occurrences of methane, either in overburden and bedrock wells, are observed within the region of Alliston- Bolton and Newmarket-Aurora. Methane concentrations reach values as high as 4500 umol/l (methane saturation in water is 1310 umol/l at 25°C). These data show high concentration of methane in overburden wells underlain either by limestone or shales. A similar pattern is observed in bedrock wells.

A common tracer used to provide information about the origin of methane in groundwater is ^{13}C, a stable carbon isotope. The occurrence of isotope effects during reactions imprint the gas with a ^{13}C isotopic composition that is characteristic of the process responsible for the formation of methane. Biogenic methane, excluding gases generated in landfills, are characterized by $\delta\ ^{13}C$ values less than -60 o/oo, whereas thermocatalitic methane have values greater than -45 o/oo.

The $\delta\ ^{13}C$ values for methane samples from the Alliston aquifer range between -70 o/oo to -84 o/oo, with most of the values around -75 o/oo. No significant isotopic differences have been found in methane from overburden and bedrocks wells. This isotopic range is typical of biogenic methane. In addition, deuterium (^2H),an hydrogen stable isotope have been analyzed in methane samples to provide information about the origin of methane and the type of reactions that are involved in the methane formation. The ^2H results from methane and also groundwater indicated that about 80 o/oo of the methane is formed by CO_2 reduction and the remaining 20 o/oo by acetate fermentation.

Potential carbon sources for the generation of methane in the Alliston aquifer complex are organic matter present in the aquifer material and bedrock and dissolved organic carbon in the groundwater.

DOC concentrations in the groundwater range from 1 ppm to values as high as 17 ppm. Typical DOC concentration are less than 1 ppm in deep groundwater and less than 5 pppm in unconfined aquifers in the Alliston area. These high DOC concentration suggest that the groundwater is moving through aquifer materials that are rich in organic matter. An excellent linear correlation was found between DOC and methane concentration for overburden wells. This correlation is not so clear for bedrock wells. A plume of high DOC seems to correspond with the areas of high CH_4 concentration. This correlation suggest that DOC and CH_4 are related to a common carbon source. This hypothesis is been tested by ^{14}C dating on DOC and CH_4 samples. Preliminary data show a very similar radiocarbon age range for DOC (30,000 and 22,000 yr B.P) and CH_4 (40,000 and 30,000 yr B.P) in some overburden groundwater, however in other overburden wells, radiocarbon ages for CH_4 are similar (30,000 yr B.P), but the DOC is much younger (16,000 yr B.P). The only data from a well in limestone shows a similar age to overburden wells for CH_4, but DOC is significantly much younger (5,000 yr B.P). These data clearly indicate that at least one of the carbon sources for both carbon pools must be present in the aquifer sediments, since the other possible carbon source, shale and the limestone bedrock, are devoid of ^{14}C atoms.

Evidence of existence of organic matter (black muck) in aquifer material have been found in water log records published by the M.O.E. Deposits of organic rich sediments (peat) have been confirmed by a driller in the area of Schomberg. The groundwater in this area is characterized by high concentration of methane. This additional information support the idea of the existence of a carbon source for the methane within the aquifer sediments.

The possibility than methane is associated with older groundwater is also being investigated using ^{18}O and ^{2}H analyses in the groundwater and ^{14}C and ^{13}C in dissolved inorganic carbon. This data shown an isotopic range between -14.3 o/oo and -10.7 o/oo for ^{18}O and -92 o/oo and -78 o/oo for ^{2}H. This is a significant isotopic difference and implied that at least two types of groundwater are present in the aquifer. The isotopic composition of modern groundwater in an unconfined, shallow aquifer in the Alliston area, ranges between -10.8 o/oo and -11.5 o/oo for ^{18}O and -73 o/oo and -81 o/oo for ^{2}H. The presence of isotopically depleted groundwater (δ ^{18}O =-14.3 o/oo in case of the Alliston aquifer) implies that these waters were recharged under cooler climatic conditions than today.

A number of conclusions can be made on the basis of our results to date: CH_4 in the aquifer is formed by microbial processes, and is not thermocatalitic, as is the case for many bedrock CH_4 sources in Southern Ontario; The nature of the Paleozoic bedrock does not control the distribution of CH_4 in the aquifer; CH_4 and DOC appear to be linked to a common organic rich carbon source present in some parts of the aquifer; and, some parts of the aquifer contain very old groundwater that was recharged under cooler conditions than at present or reflected the input of glacial meltwater.

Our present and future research will focus on the completion of geochemical evaluation of CH_4, DOC, and geochemistry of representative overburden and bedrock groundwaters. We will also evaluate the nature of the aquifer sediments, with an emphasis on the tills and organic units. This will be done in areas where especially high concentration of CH_4 and DOC are found, and where we have found evidence of buried inter-glacial peat deposits. All geochemical, geological, and hydrological information will then be synthesized to produce an acceptable model for the origin, occurrence, and prediction of CH_4 in the Alliston aquifer complex.

BP5

MICROBIAL METHYLATION OF MERCURY IN ACID STRESSED LAKES - ROLE OF SULPHATE REDUCING BACTERIA

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INTRODUCTION

Elevated levels of mercury have recently been detected in fish from acid stressed and other softwater lakes of the Muskoka-Haliburton region in south-central Ontario, Canada. 95% of the lakes in this region contain sport fish that are above the guideline for unrestricted human consumption. There is no clear source of mercury contamination in this area and thus no abatement measures have been implemented. This non-point source mercury contamination may be due, in part, to long range atmospheric transport of mercury from combustion sources.

Some of the occurrences of the elevated mercury levels in fish tissue, in lakes removed from point sources, appear to be related to the acidity of surface waters (Sloan & Schofield, 1983; Wiener, 1983; Wren & MacCrimmon, 1983; Bjorklund et al., 1984; Suns et al., 1987; Hakanson et al., 1988). Other factors, such as the supply of organic carbon (Bodaly et al., 1984; Hecky et al., 1987; Jackson, 1988), the form and availability of mercury (Rudd & Turner, 1983), the presence of humic and fulvic acids (Mannio et al., 1986; Surma-Aho et al., 1986), and the amount of sulphate present (Compeau & Bartha, 1985; Gilmour & Mitchell, in press), are also statistically related to the level of fish mercury.

Mercury readily accumulates in muscle as well as other tissue of fish and is biomagnified in the aquatic food chain (Huckabee et al., 1979). Methylation of mercury by microorganisms produces a form of mercury that is more toxic and more biologically available to biota than is inorganic mercury (Beijer & Jernelov, 1979). Microbial communities in lake sediment are known to methylate inorganic mercury and logically, factors which change or stimulate portions of this community can influence the rate of methylation (Summers & Silver, 1978). It has been suggested, based on estuarine studies, that one group of sediment microbes, the sulphate-reducing bacteria, may be significant methylators of mercury (Compeau and Bartha, 1985). It was previously proposed that methanogenic bacteria were responsible for the major amount of mercury methylation (Wood et al., 1968; Jensen & Jernelov, 1968).

The increased input of sulphate from acidic deposition may stimulate sulphate-reducing bacteria over the other sediment populations thereby potentially increasing the rate of methylmercury production in the system. The objective of our study was to elucidate the possible role of freshwater sulphate-reducing bacteria in methylmercury production and to determine the effect that sulphate input can have on their activity. The role of freshwater sulphate-reducing bacteria from the Muskoka-Haliburton area (Dickie Lake, pH 5.7) in methylmercury production was examined by adding specific microbial inhibitors to anoxic lake sediments spiked with $^{203}HgCl_2$. The effect of increased sulphate on the activity of sulphate-reducing bacteria both in terms of sulphate reduction rate and methylation of mercury was examined by adding appropriate ranges of concentrations of sulphate to $^{203}HgCl_2$ spiked sediments.

MATERIALS AND METHODS

Dickie Lake in the Muskoka-Haliburton region of south-central Ontario, Canada (Latitude 45° 09'N, Longitude 79° 05'W) was sampled regularly to provide sediment and water. The pH of the lake ranged from pH 5.7 to 6.0 with an acid shock event (pH 5.1) at snowmelt. The sediments were sandy with low organic content (Loss on Ignition, 450°C for 4 hrs, was 1-4%) and the lake water had a sulphate concentration of 6-8 $mg.L^{-1}$.

Sediments were collected from the epilimnion near the outflow of Dickie lake. Cores (10 by 50 cm) were taken by hand at a depth of 1-2 m in replicates of six. The cores were then packed on ice and transported to the laboratory where they were preincubated at 25°C for 2 weeks before use. Cores were extruded and manipulated in an anaerobic glove box filled with flowing oxygen-free nitrogen gas. After the top 1 cm of floc had been removed, the subsequent 5-10 cms of anoxic sediments were pooled from at least 3 cores. Sediment slurries were made with a medium designed to approximate the low-alkalinity waters of acid sensitive lakes in the study area, Muskoka medium (Wehr and Brown, 1985), with the following modifications: sulphate content was lowered to 3 $mg.L^{-1}$, vitamins were eliminated, and 0.5 $g.L^{-1}$ of yeast extract was added. A slurry was made of 1 part sediment to 3 parts Muskoka medium. Forty ml aliquots were dispensed into 60 ml serum bottles and sealed with butyl rubber stoppers (Compeau and Bartha, 1985).

All reagents were then added by syringe into the sealed bottles outside the anaerobic glove box through the respective septa.

Specific rates of mercury methylation were determined using the radiochemical method of Furutani and Rudd (1980). 1 µCi of $^{203}HgCl_2$, approximately 1 µg of Hg, was added to each 40 ml sample bottle through the septum (approx. 67 ng per dry sediment) and incubated at 25°C. At the end of the experiment, 1 ml of 4N HCl was added to stop the biological reaction and alkylated ^{203}Hg was extracted from the total contents of the bottle (Furutani and Rudd, 1980). The alkylated ^{203}Hg, extracted into toluene, was then dried with Na_2SO_4 to remove excess water and determined on a gamma counter. All experiments were done with at least 3 replicates at each condition along with three acid-killed blanks (1 ml of 4N HCl added to bottle). The extraction efficiency of the technique was assessed by using the methylated isotope, $CH_3{}^{203}Hg$; extraction was 78-80% efficient. All calculations were corrected accordingly.

RESULTS & DISCUSSION

Both sulphate-reducing bacteria and methanogens were present in the anoxic sediment of Dickie Lake. Specific microbial inhibitors, that were added to ^{203}Hg spiked slurries, were effective in inhibiting the target microbial population, i.e. $NaMoO_4$ inhibited sulphate-reducing bacteria and BESA inhibited methanogenic bacteria. $NaMoO_4$ decreased methyl-mercury production by 75% but BESA did not significantly decrease methylmercury production (Figure 1). Varying levels of inhibitors; 5, 10, 20 mM NaMo and 7.5, 15, 30 mM BESA, produced the same pattern as shown in Figure 1 independent of concentration. This indicates that sulphate-reducing bacteria are the main methylators of mercury in these sediments under the experimental conditions that are used.

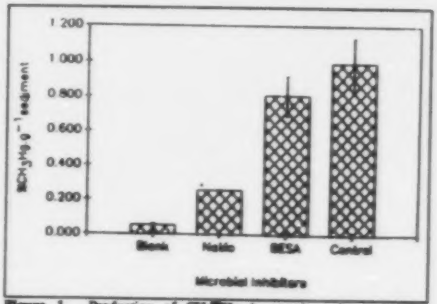

Figure 1. Production of $CH_3{}^{203}Hg$ in anoxic sediment slurries (Blank = Acid killed, NaMo = 10 mM Na_2MoO_4, BESA = 15 mM 2-Bromoethane sulfonic acid,Control = no additions).

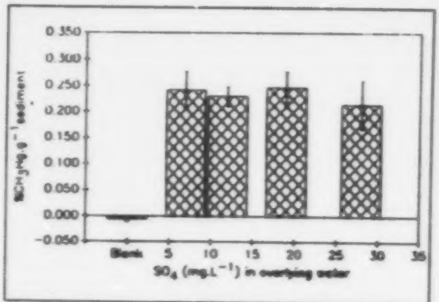

Figure 2. Production of $CH_3{}^{203}Hg$ in anoxic sediment slurries over the naturally occurring range of sulphate levels found in the experimental area.

The rate of sulphate reduction from the water overlying the sediment slurries increased as the concentration of sulphate in the water increased. This indicates that the resident population of sulphate-reducing bacteria are stimulated by small inputs in sulphate to the water column. However, the increase in activity of the sulphate-reducers did not correlate with increased production rates of methylmercury. Across the range of sulphate concentrations tested, there was no significant difference in the amount of methylmercury produced (Figure 2). Therefore the stimulatory effect of sulphate on these bacteria does not seem to be translated into increased methylation rates of mercury.

CONCLUSIONS

Under our experimental conditions, sulphate-reducing bacteria do appear to be major methylators of mercury in freshwater, anoxic sediments and were more important in this respect than methanogens. However, the stimulatory effect of sulphate, within normal levels, on these bacteria's ability to further methylate mercury remains unclear.

ACKNOWLEDGMENTS

We would like to thank the Ontario Ministry of the Environment for funding this project. Thanks also go to Brenda Miskimmin, Miriam Diamond, SLOWPOKE reactor facility, Dr. T.C. Hutchinson, Matt Hilgerdenaar, and Dr. G. Mierle for all his intellectual and technical input.

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BP6

INFLUENCE OF LAKE pH AND MACROGRAZERS ON THE DISTRIBUTION AND ABUNDANCE OF NUISANCE METAPHYTIC ALGAE IN CENTRAL ONTARIO, CANADA

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Abstract

Thirty six softwater lakes in central Ontario were sampled during 1988 to determine (a) the relationship between metaphytic Zygnematacean algae and lake pH, and (b) the degree of complementarity between the presence and abundance of metaphyton and that of crayfish and tadpoles. Below pH 6.0, a greater proportion of the lakes had extensive metaphyton than above pH 6.0. Lake pH and alkalinity respectively were significantly correlated with metaphyton abundance. We recommend incorporating an index of metaphyton abundance into the biological assessment of acid sensitive waters. No significant relationship was shown between presence and absence of metaphyton and macrograzer (tadpoles or crayfish) density, but a relationship was seen between the degree of metaphytic development and macrograzer density in those lakes that were already predisposed to metaphyton development. Implications for management of the nuisance algae by stocking crayfish and/or tadpoles, is considered.

Introduction

In a recent survey for the Ontario Ministry of the Environment of more than 500 cottagers on recreational lakes in the Parry Sound-Muskoka-Haliburton regions of central Ontario, the researchers concluded that approximately half of the lakes had "some" development of filamentous algae and that about 16% of them had "considerable" accumulations (SPR 1986). The free floating mats of benthic algae that are of major concern are classified as metaphtyon (Wetzel 1983). Because of the socioeconomic significance of these nuisance algal communities, and because there is evidence (e.g. Stokes 1986) that the proliferation of metaphyton can be an acid-related phenomenon, any understanding of the mechanism(s) involved in the proliferation of the community would have practical as well as scientific interest.

The present study was set up to address the following objectives:

1. To provide a quantitative assessment of the extent and abundance of metaphytic algal clouds in a survey of lakes in central Ontario ranging from pH 5.4 - pH 6.6. An ancillary to this was to design a cost-effective but reliable sampling protocol to facilitate the use of the community as a biomonitor of acidification (Stokes and Howell 1987).

2. To determine whether there was a relationship between macrograzer density and metaphyton abundance, given that one of the hypothesised mechanisms for the phenomenon is reduction or loss of invertebrates or small vertebrates from acidic lakes, resulting in release from grazing pressure.

Methods and approaches

Lakes that were sampled were selected based on the following criteria: they were oligotrophic, acid sensitive, relatively clear (<90 Hazen units), not excessively large or small and had been described previously as having metaphyton based on cottager surveys (SPR 1986) or direct assessments by the Ontario Ministry of the Environment (Jackson unpublished).

For sampling, the lake perimeter was divided into a series of small zones representative of points, bays and straight shoreline respectively. Within each of those strata, precise sampling locations were chosen at random. Two types of sampling were used to assess metaphyton abundance: box quadrat (destructive) sampling, followed by measurements of wet biovolume and dry biomass. A visual classification of aereal cover was based on seven categories: "nil", "detected", "present", "rare", "common", "abundant" and "very abundant".

Macrograzers were sampled in minnow traps baited with fish-flavoured cat food, beef-flavoured dog food and boiled macaroni.

Results and Discussion

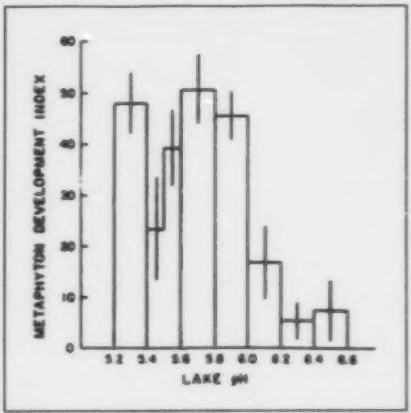

Figure 1. Relationship of lake pH to development of metaphyton for 36 lakes.

Ranked designations of metaphyton abundance were closely related to lake mean biovolume or biomass (Fig. 1). This provides the basis of a cost-effective technique enabling teams of workers on a fairly large number of lakes to quantitatively and objectively measure metaphyton development in a survey mode. There was relatively good agreement between this quantification of metaphyton and of its recognition by the cottagers in the questionnaire survey (SPR 1986).

Statistical analysis of the data suggested that lake pH, alkalinity, total nitrogen and crayfish abundance might be related to metaphyton development. The best match was for pH and alkalinity respectively with metaphyton abundance (Fig. 2). Ranked pH and alkalinities were significantly ($P<0.01$) correlated with ranked metaphyton biovolumes and biomass.

Metaphyton abundance was negatively related to abundance of macrograzers, but this effect was secondary to the dominating influence of lake alkalinity or pH. Figure 3 shows the relationship between ranked macrograzer abundance and metaphyton abundance for those lakes (23) that contained filamentous algae.

Two anomalous lakes contained both abundant grazers and abundant metaphyton. These two lakes (Heney and Maniwaki) were far more shallow than the other lakes with high metaphyton biovolumes.

In general then, it remains unclear whether the metaphyton abundance in softwater lakes is controlled by the direct effect of pH (see e.g. Howell 1988), by the abundance and resulting grazing pressure of grazers, or by both. Therefore projections concerning biological control of the nuisance algae are premature. However, there is sufficient evidence for the role of grazers as controlling factors to recommend more detailed studies on the mechanism with respect to the relationship between the respective abundance of grazers and metaphyton.

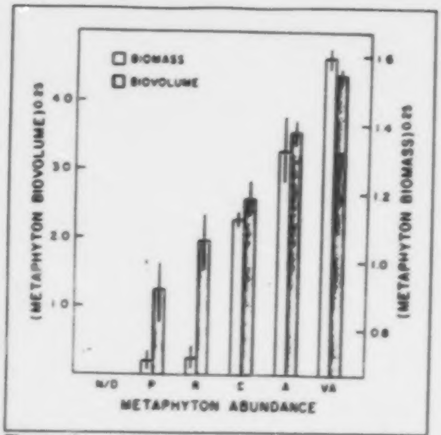

Figure 2. Relationship between ranked metaphyton abundance from sequential sampling program and mean lake biovolume (ml/m²) and biomass (mg/m²).

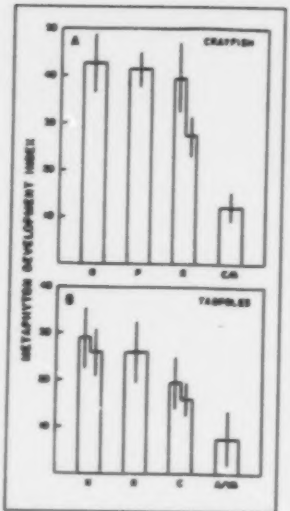

Figure 3. Relationship of ranked abundance of crayfish and tadpoles to metaphyton development.

Acknowledgements

The work was funded by the Ontario Ministry of the Environment. We wish to acknowledge in particular the contribution of Michael Jackson, and the chemical analyses that were done by permission of Peter Dillon. Research assistance was provided by K. Adare, J. Robbins, S. David and M. Dennison, and N. Flood provided statistical advice. The senior author was supported by a Natural Sciences and Engineering Research Council of Canada Post-doctoral Fellowship.

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BP7

ASSESSMENT OF FECAL POLLUTION TRANSPORT IN AGRICULTURALLY IMPACTED WATERSHEDS USING A BIO TRACER; M. Walters, and E. Harris, Lake Simcoe Region Conservation Authority, Newmarket, Ontario, L3Y 4X1.

In May, 1988, the Lake Simcoe Region and Metropolitan Toronto and Region Conservation Authorities began research on the travel times of fecal indicator bacteria in rural watersheds. The study was initiated to provide much needed data for transport modelling exercises currently in progress as part of the Provincial Rural Beaches Strategy Study. The development of simple models for evaluating source inputs and transport of pollutants were considered essential for the watershed remedial action strategies. The prime purpose of the hydrologic transport model is to establish the potential boundaries of impact of source(s) on beach areas.

Two streams were selected for examination: Pefferlaw Brook, in the Lake Simcoe region, and Centreville Creek, in the Metro Toronto region. Only a portion of each stream was considered suitable for conducting bio tracer experiments. In Pefferlaw Brook, the reach selected was 22.25 km in length, and comprised an area of approximately 160 square km from the brook's headwaters to a point above its confluence with Uxbridge Brook. In Centreville Creek, the study area included a 6.95 km section of the creek from a point below Innis Lake and Belcon Pond to the Albion Hills Pond. Recreational beaches were located in the downstream portion of both study areas.

Preliminary analyses in the selected reaches of both watersheds were made in May, 1988, using fluorescein dye. A concentrated solution of the dye was added to the water column in the upstream areas of the study reach, and was tracked downstream by both direct observation and fluorescence measurement using a Turner T1101 fluorometer. These initial dye tracer experiments were conducted to determine travel times within reach areas so that sampling sites could be established.

A Nalidixic Acid resistant strain of *Escherichia coli* originally isolated from the environment by G. Palmateer (Ministry of the Environment, London) was selected for use to study instream bacterial movement, and sediment bacterial transport . The strain is considered ideal for use as a biological tracer because it is non-enteropathogenic, easily recovered from water and sediments, and not commonly found in the environment.

Water column and sediment samples were collected from various points along the tracer route, and analyzed to ensure that the Nalidixic Acid resistant *E. coli* strain was not normally present in the two watersheds. This negative check was repeated before the start of each tracer run to confirm that the tracer organism was not present within the stream system before new tracer bacteria were added.

Water column tracer runs involved the growth of large batch cultures of the tracer *E. coli* which were transported to the injection point and mixed with a fluoroscein dye solution before being introduced into the stream. The bacteria/dye suspension was then

tracked by sampling the plume at predetermined points downstream. The sampling procedure was designed to measure the peak concentration over time and involved taking a series of sample sets, each set being comprised of three samples taken across the stream section. Sampling procedures followed guidelines set by the Ministry of the Environment's Laboratory Services Branch. Mohr swabs were employed to assess if resuspension of the tracer organism was occurring within the reach areas. Swabs were placed at the sampling sites a day after the plume had passed and sampled twice weekly for a two week period. Sediment tracer runs required that sediments from the two creeks bottoms were collected and seeded with the bacterium and replaced on the stream bed. Water, sediment, and swab samples were then collected from downstream areas over time.
Field experiments comparing the instream survival characteristics of the tracer with other E. coli strains were also performed using in situ environmental diffusion chambers (McFeters et. al., 1972). Bacteria survival is one of the many instream processes occurring during bacterial transport which could be readily measured. Water column survival experiments were conducted during July and August each experiment lasting approximately three weeks in duration. The experiments were conducted in both watersheds utilizing sampling sites located within the reach areas.

A total of 9 water column and 2 sediment tracer runs were conducted in the two watersheds during the summer and fall of 1988. Results from water column bio tracer runs show the average travel time of E. coli in Pefferlaw Brook to be 2.5 days, and 0.9 days in Centreville Creek, under summer flow conditions. Calculation of the total travel time of the tracer bacteria through each watershed was made by determining the time at which the peak of the tracer plume passed through each site, and adding these values together.

The survival characteristics of the bio tracer were found to be similar to other strains of E. coli, exhibiting instream survival for approximately a two week period. Die-off of rates for the bio tracer were slightly higher than those recorded for E. coli (0.2210 log units per day decrease for bio tracer versus a 0.1982 log units per day decrease for E. coli). Based on these findings alone it is apparent that even the most distant pollution inputs in these two watersheds would impact on downstream beach areas. The significance o. the source contribution being a function of the time of travel and the survival rate of the bacteria.

Massive decreases in the peak concentrations of the Nalidixic Acid Resistant E. coli was observed between downstream sampling stations during the water column tracer runs which could not be attributed to bacteria die-off alone. The results indicated that other instream processes such as deposition were actively affecting the instream pollutant transport process. This theory was supported by sample results which found low concentrations of the tracer organism in bottom sediments and the reoccurrence of the Nalidixic Acid Resistant E. coli on Mohr swabs as deposited tracer was resuspended. Information obtained from sediment tracer experiments, suggest that sediments can act as reservoirs and prolong the period over which a pollution input will impact on downstream areas.

BP8

Sediment Transport Model, Research and Implementation; W.P. Hollarum and M.D. Palmer, Beak Consultants Ltd., Brampton, Ontario and R.J. Dewey, Gore and Storrie, Toronto Ontario

Paper withdrawn

BP9

IN SITU DETERMINATION OF FECAL INDICATOR BACTERIA SURVIVAL IN AGRICULTURALLY IMPACTED WATERSHEDS; E. Harris, and M. Walters, Lake Simcoe Region Conservation Authority, Newmarket, Ontario.

Research on the in stream survival characteristics of fecal and water quality indicator bacteria was initiated in the summer of 1987 by the Lake Simcoe (LSRCA) and Metropolitan Toronto (MTRCA) Region Conservation Authorities. The 2 1/2 year study was designed to provide data on bacterial die-off rates in waters primarily impacted on by agricultural pollution inputs. Information on bacterial die-off was determined necessary for the development of hydrologic transport models to establish the potential boundaries of impact of sources on beach areas in rural watersheds. Transport modelling exercises are currently in progress as part of the Provincial Rural Beaches Strategy Study, a cooperative program between the Ontario Conservation Authorities, and the Ministry of the Environment.

Six locations within the confines of the LSRCA and MTRCA Rural Beaches Study areas were selected for examination. These included: 3 sites in Pefferlaw Brook (LSRCA), 1 site in the East Humber River (MTRCA), and 2 sites in Centreville Creek (MTRCA). The bacterial parameters examined included: Escherichia coli (EC), fecal coliforms (FC), fecal streptococci (FS), and Pseudomonas aeruginosa (PSA).

Water column die-off rates of these bacteria were assessed under four seasonal conditions: summer, fall, winter, and spring. Survival characteristics of EC and PSA in stream bed sediments were also determined under all seasonal conditions. In addition to the survival experiments, monthly samples of bed sediments at each site, were analyzed for the per gram concentrations of FC, EC, FS, and PSA. A total of 228 water column, and 50 sediment survival runs were conducted during the 2 year field component of the study.

The methodology for conducting survival experiments incorporated the use of 50 millilitre volume membrane diffusion chambers, developed by G. McFeters of the Montana State University, (McFeters and Stuart, 1972; 1981). The chambers were made of plexiglass with 0.2 micron polycarbonate filter side walls (Millipore), and allow for maximum exchange with the aquatic environment, while retaining the test bacteria as a separate entity. Further modifications to the current method, including the design of the sediment and water column chamber holders, were made by G. Palmiteer of the Ministry of the Environment, London, Ontario.

Chambers for water column runs were inoculated with test bacterial cultures, diluted ten fold in both sterile and non sterile site water. The bacterial cultures used were originally isolated from the LSRCA and MTRCA watersheds, and were grown to mid stationary phase in nutrient broth prior to dilution. Time zero control samples were taken from inoculated chambers, and analyzed to determine the initial bacterial concentration. Generally, starting concentrations ranged between 10,000 and 100,000 bacteria per ML.

Sediment survival chambers were prepared by inoculating 5 mL of an EC or PSA culture (as prepared above) into chambers containing 50 grams of both sterile and non sterile stream bed sediment. Again, time zero control samples were analyzed to determine initial concentration. The starting concentrations in sediment chambers ranged from 1000 to 10,000 bacteria per gram (wet weight).

All chambers were transported to the field locations in sealed containers of chilled (4 degree celsius) site water, and placed into anchored plexiglass holders. Triplicate water column chambers were placed at each of the six sites. These were sampled over a two to three week period by withdrawing small volumes of the bacterial suspension from the chambers using sterile luer lok syringes. Samples were taken daily during the first week, and twice per week thereafter. Sediment chambers were sampled over a seven week period by removing 1 chamber per site at 24 and 72 hours, and once per week during the remaining six weeks. Monthly bed sediment samples were collected in sterile glass jars. Only the top 2 inches of the stream bed were removed for analysis.

Chamber and bed sediment samples were transported to the laboratory on ice, and analyzed within 24 hours for bacterial concentration by membrane filtration or most probable number methods, using current Ministry of the Environment media and techniques.

Physical and chemical characteristics of the water column were measured during each survival run. These parameters included: Temperature, turbidity, pH, conductivity, DOC, TP, TKN, No3, NO2, and AMM, Bed sediment samples were typed according to particle size, and levels of nutrients. The effect of these parameters on bacterial survival have not been fully assessed due to the fact that some of the test results are still outstanding.

Bacterial die-off rates for both water column and sediment survival runs were calculated by linear regression analysis of log bacterial concentration with time.

Results of the water column survival experiments show that overall, bacterial die-off rates in the three watersheds fell within a range of 0.1 to 0.5 log units per day decrease. Previous studies on bacterial survival (Seyfried, Harris, and Young, 1986 unpublished) have reported more rapid instream die-off rates in urban waters than those observed in these rural streams (ie. 0.5 to 1.0 log units per day decrease). Significant variability in the rates was noted between seasons, sites, and bacterial parameters, such that definite patterns could not be established. However, slight trends were noted. For example, a tendency towards more rapid die-off of FC and EC was observed during summer, while some of the slowest rates for these organisms were displayed during winter. Pseudomonas declined more slowly than either FC or EC under most environmental conditions. Fecal streptococci showed similar die-off characteristics to that of FC.

Increased nutrient levels in the water tended to prolong bacterial survival, especially during the warmer summer months. Pseudomonas was observed to exhibit regrowth in more nutrient enriched waters (ie. areas such as cattle access sites), at temperatures as low as 15 degrees celsius. The results of using sterile and non sterile water as the diluting medium for the bacterial cultures, tended to confirm the effect of increased nutrient levels on bacterial survival. Sterilization by autoclaving, raises the level of available nutrients in the water. Bacterial die-off rates determined from survival runs using sterile water were one half as slow as the rates computed from runs where non sterile water was used.

Die-off of both EC and PSA in sediments proceeded at a much slower rate than in the water column (ie. 0.05 to 0.3 log units per day decrease). This was most likely due to the fact that sediments are more nutrient enriched than water and therefore, would facilitate extended bacterial survival. Regrowth of both bacteria occurred during the summer in chambers containing sterile sediments. Again, this would be the result of the increased availability of nutrients present in autoclaved sediments.

Results of the monthly sediment analyses revealed that levels of fecal and water quality indicator bacteria in stream bed sediments were low (ie. < 100/gram) during the fall, winter, and spring months, but that per gram concentrations of these organisms could rise during the summer. Levels of FC, EC and FS increased to between 200, and 1100 per gram at some sites.

In summary, the conclusions drawn from the study were that indicator bacterial die-off in the three rural watersheds was quite slow, and thus would not account for any significant decrease in downstream loadings to beach areas. Increased nutrient levels from agricultural inputs to these surface waters, especially under warmer water temperature conditions, could result in even more prolonged survival of the bacteria. A potential for accumulation and temporal extension of pollution problems exists due to the slow die-off of indicator bacteria in stream bed sediments. Finally, based on the variability in rates demonstrated between sites, bacterial die-off is site specific, and the rates observed in one watershed cannot be applied to other water bodies.

BP10

ABSTRACT

The Effects of Agricultural Drainage
on
Sediment and Water Quality Loadings

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INTRODUCTION

Impairment of water quality as a result of agricultural activity is desired neither by the farming community nor by recreational users of receiving water bodies. Removal of valuable pesticides, fertilizers and topsoil by surface or subsurface drainage represents an economic loss to agriculture and a potential pollution hazard to receiving waters. In order to evaluate this potential impairment of water quality, there is a need for accurate prediction of chemical contaminant and sediment loadings for different environments, loading conditions, and agricultural management strategies. Such an evaluation is best accomplished by a combination of selective measurement and more general modelling. The model employed should be deterministic and capable of simulating both water quantity and quality at the field level. A few quantity models that meet these criteria are available. However, because of the lack of applicable quality models, a major task in this project is the development of physically-based quality algorithms that can be linked to hydrologic quantity models to accurately predict chemical contaminant and sediment loadings.

OBJECTIVES

After consideration of the state-of-the-art in quality simulation as it relates to agricultural watersheds, the following research objectives were defined:

1) definition of the processes involved in movement in contaminants through the soil or over the surface and into the tiles or ditches draining agricultural fields,

2) incorporation of an understanding of these processes into a physically-based model capable of simulating water quality changes on a basin scale,

3) collection of field data for calibration and verification of the model,

4) use of the model to evaluate the effects of tile drainage on sediment and water quality loadings, and

5) provision of guidance on the use of the model for evaluation of potential management strategies.

METHODS

During 1989, simple algorithms to represent processes for chemical transport through the soil profile and into the tile drains were developed. These algorithms were incorporated into TILE which is a continuous, physically-based hydrologic simulation model for tile-drained agricultural fields and basins. The comentations and loadings of nutrients and pesticides can be traced through the soil profile to the tile drains or on the surface as ponded water or surface runoff.

To obtain data upon which to test and calibrate the model, a co-operative field program was entered into with Agriculture Canada to monitor tile water quantity and pesticide concentrations from a tile-drained corn field at the Ottawa Experimental Farm. Volumes and rates of runoff were monitored over the 1989 season on a continuous basis. Concentrations and loadings of nutrients and pesticides were determined under significant runoff events through the use of a flow-activated water quality sampler.

In addition to the monitoring of the runoff, field studies were undertaken to define the physical parameters required by the model -- saturated hydraulic conductivity, soil type and depth, drainable porosity, infiltration characteristics -- field slopes and tile installation details.

Following the collection and reduction of the water quantity data from the field, TILE was calibrated to ensure it would accurately reproduce the hydrologic response of the tile-drained field. Preliminary testing of the water quality algorithms for the pesticide employed (metolachlor) was undertaking.

Work in the final year of the project will involve the finalization of algorithms for water quality transport models and the testing of agricultural management practices as they may influence nutrient or pesticide loss from the fields through the tile drains.

BP11
Manuscript not submitted.

TRENDS ANALYSIS PROCEDURES FOR WATER QUALITY TIME SERIES. A.I. McLeod*, Dept. of Statistical and Actuarial Sciences, the University of Western Ontario, London, Ontario N6A 5B9, K.W. Hipel, Dept. of Systems Design Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, and B. Bodo, Water Resources Branch, Ontario Ministry of the Environment, 135 St. Clair Avenue West, Toronto, Ontario M4V 1P5.

A general methodological approach is developed for detecting and modelling trends in water quality time series. Trend analyses are required for alerting authorities about water quality degradation so that appropriate corrective action can be taken and for evaluating the performance of pollution abatement schemes. The general approach to trend assessment includes examining a graph of a given water quality series time series along with a robust locally weighted regression (RLWR) smooth through the graph, using RLWR to remove the effects of riverflows upon the water quality series to obtain flow adjusted data, checking for the presence of seasonality in the flow adjusted data, employing appropriate nonparametric and parametric tests to identify trends, and properly accounting for trends that may be present in the riverflow data. To demonstrate how the trend analysis methodology is used in practice, it is applied to a variety of water quality and water quantity times series from the Saugeen and Grand Rivers in Southern Ontario.

BP12

GREYWATER DISPOSAL FROM PLEASURE BOATS

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Description of the Study

The objectives of the study were to estimate the wash water bacterial loadings from recreational boats and whether these loadings could cause bacterial densities to exceed acceptable levels for recreational swimming. To determine a representative loading from recreational boats the different types of boats and types of crews must be considered over a long enough period of time to obtain a meaningful result. Three types of boats were used; namely, a houseboat, power cruiser and sailboat. Each boat was modified so that all the wash water was collected in a tank and the tank was sampled twice daily. Each sample was stored in a cooler on ice and delivered to a laboratory within 24 hours for ennumeration of fecal coliform (FC) and E. coli. (EC). A crew stayed on each type of boat for five or six days. The composition of the crews varied from four single adults to two couples and couples with children. All crews consisted of at least four people.

To determine the impact of the wash water discharges on receiving waters, the power cruiser and sailboat were moored in confined popular embayments on Georgian Bay namely Lost and Frying Pan Bays on Beausoleil Island and the houseboat was moored at Blind Channel on the Trent River waterway. Bacterial samples were collected in the embayments throughout the day at selected locations to assess the impact of the wash water discharges. Currents were also measured and the number of boats were noted during each sampling run.

RESULTS

Wash water Characteristics

All of the results based on presumptive bacterial testing procedures indicated very high densitites of FC and EC in the wash waters. Differences between types of boats and fixtures (head sink, galley sink, shower) were not statistically significant at the 95 percent confidence level. FC and EC mean densities ranged from 10^5 to 10^9 organisms/100 ml. The densities of FC and EC in domestic untreated sewage are typically about 10^7/100 ml. The wash water is a source of bacterial contamination for recreational waters if conventional analytical techniques are used although it is known that there are no sources of human fecal matter in the wash waters. Using more specific taxonomy methods on a subset of samples, only 61% of the 16 positive FC samples were identified as true FC. Of the 50 isolates identified as EC only 6% were identified as being true EC with Enterobacter sp. identified as the most common EC at 58%. High densities of Pseudomonas aeruginosa were also found in the wash water ranging from 10^2 to 10^6 organisms/100 ml. More specific taxonomic analysis on a subset of samples resulted in 100 percent confirmation of this organism.

The mean daily production per person of wash water was found to vary between 16.6 and 21.7 L.

Wash Water Discharge Impacts

The wash waters were found to have very high densities of FC and EC however, the volume of wash water discharged is small. Receiving water measurements were made in two popular confined mooring embayments on Beausoleil Island. The embayments have a surface area of approximately 10,000 to 12,500 m^2 and water volumes of from 40,000 to 90,000 m^3. The entrance to the embayments is very small (see Figure 1). Consequently, the water exchange in and out of the embayments is restricted. From measurements at the entrances, the water residence time in the embayments ranged from 8 to 36 hours. Figure 2 shows the FC and EC measurements in the embayments during a summer weekend and the number of boats in the embayments as well as the background bacterial densities based upon measurements near the entrances to the embayments. This figure clearly shows that the densities in the receiving water exceed the recommended guideline of 100 FC/100 mL for recreational swimming due to wash water discharges. The study on the Trent River mooring at Blind Channel showed similar results but the receiving water bacterial densities were not as high as those observed in the Bays because the number of boats at Blind Channel were about a third of those in the Bays during the study.

Simple statistical relationships relating boats to observed receiving water bacterial densities were not found to be significant. A deterministic mass balance water quality model relating embayment volume, exchange flow, presence of boats, bacterial decay, and background bacterial concentrations was developed and applied to the survey results. The model was found to adequately reflect embayment bacterial levels given the observed boat densitites when tested using the fecal coliform data.

CONCLUSIONS

Wash water discharges from recreational were found to have very high densities of fecal coliforms and E. coli. Although the volume of wash waters discharged per day per person was between 16.6 and 21.7 L, a large number of boats moored in confined embayments caused the fecal coliform densities to exceed 100 FC/100 mL in the embayment waters. A deterministic relationship was developed to predict the fecal coliform densities in the embayments for any number of boats provided that the water volume, water exchange in and out of the embayment and background fecal coliform densities were known.

Although, based on standard presumptive test methods, fecal coliform and E. coli densities in wash waters were found to be very high, only 3 of the 30 samples subjected to detailled taxonomy were found to be fecal in origin. These results indicate that the conventional presumptive E. coli analyses is not a good indicator of bacterial contamination from feces when applied to wash waters.

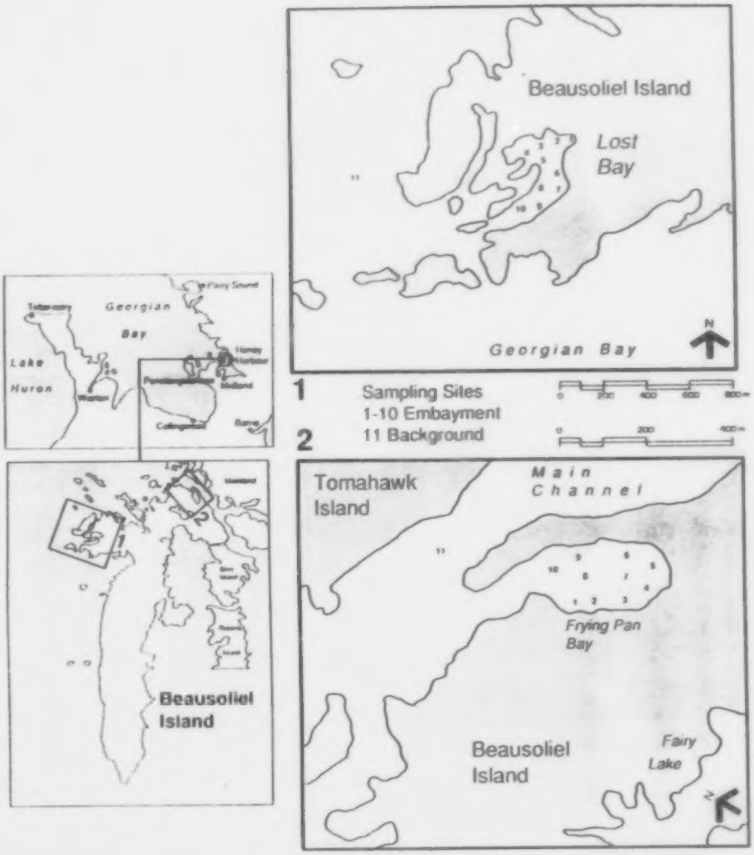
Beausoliel Island
Lost Bay
Georgian Bay
N
1
Sampling Sites
1-10 Embayment
11 Background
2
Tomahawk Island
Main Channel
Frying Pan Bay
Beausoliel Island
Fairy Lake
Parry Sound
Georgian Bay
Lake Huron
Honey Harbour
Midland
Barrie
Beausoliel Island

FIGURE 2.1
Southern Georgian Bay
Sampling Locations

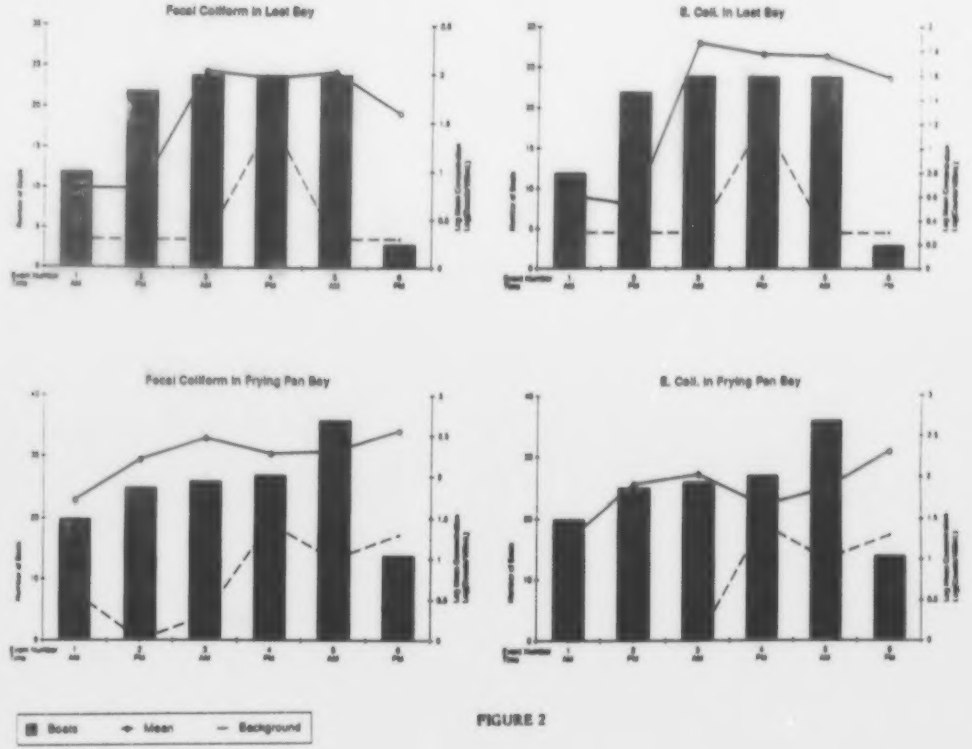
Fecal Coliform in Lost Bay
E. Coli. in Lost Bay
Fecal Coliform in Frying Pan Bay
E. Coli. in Frying Pan Bay
Number of Boats
Log Mean Concentration (colonies/100mL)
Event Number
Time
1 AM
2 PM
3 AM
4 PM
5 AM
6 PM
0
5
10
15
20
25
30
40
0.5
1
1.5
2
2.5
3
Boats
Mean
Background

FIGURE 2

B1P3

Tillage and Event Based Soil and Water Loss: Scale Linkages

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Soil erosion has been identified as a significant problem affecting water quality in Ontario. however, there have been few actual measurements. In addition the movement of dissolved chemicals in runoff water from agricultural land can also affect water quality. The variable, site specific nature of soil and water loss by runoff, as well as the lack of understanding of these processes under spatially varying field conditions has been documented.

Conservation tillage has been defined as any tillage system that reduces the loss of soil and water from a field. It is most often associated with minimum, non-inversion, or zero tillage system. The broad definition of conservation tillage is due to the recognition of significant interaction between specific soil types, climate, and tillage on runoff processes. Studies comparing one-time measurements of the effects of tillage on surface hydraulic properties may obtain contradictory results because the effects of tillage are time dependent.

Measurement of soil and water loss is difficult and is usually obtained from hillslope plots maintained over many years, or by rainfall simulation on microplots. Serious difficulties arise in attempts to transfer knowledge from laboratory or plot scale experiments to the field scale. Inability to cope with spatial variability remains a major obstacle to interpretation of research for field scale predictions.

The objectives of this study are to examine the spatial and temporal variations of soil and water loss under different tillage systems and soil types. Linkages between different spatial and temporal scales of measurement will be examined by measuring both event based losses at the plot scale, and average annual losses at the hillslope scale.

The project is being carried out on Tillage-2000 plots. Tillage 2000 is a long term, on farm, field scale research and demonstration project initiated in 1985 by the Ont. Min. of Agric. and Food and the Dept. of Land Res. Science, Univ. of Guelph. Approximately 30 field scale sites with tillage comparisons have been established. Average annual soil loss is being measured at the hillslope scale using ^{137}Cs as a naturally occurring soil tracer. Plot scale information on soil and water loss are being collected using rainfall simulation and collection of natural events using a system of runoff interception troughs and collection containers. The Guelph Portable Rainfall simulator was modified to carry out simulated rainfall on a range of plot scales from 1 m^2 to 20 m^2. The scale of the runoff plot was systematically changed during rainfall simulation and the effects on soil and water loss measurements were examined. Measurements were carried out on light (loamy sand) and textured (loam) soil, under no-till minimum, and moldboard plough tillage systems.

In the light textured soil at low rainfall intensities, total soil loss and total phosphorus loss were 54% and 30% higher in the moldboard plough compared to no-till treatment. However, actual water runoff was over 200% (double) higher in the no-till compared to moldboard treatment. Thus, considerably more, but cleaner water came off the no-till plots. The increased runoff water in the no-till could pose problems with surface transport of chemicals if they are concentrated at the surface. For high intensity rainfall, water loss was similar in the tillage treatments, but soil loss was significantly higher in the moldboard treatment. In the medium textured soil, water and soil loss on the no-till treatment was significantly lower at all rainfall intensities.

A significant interaction between scale of measurement and measured losses occurred in all of the tillage plots. For example, the steady state infiltration rate, which is suppose to be constant for a plot varied with rainfall intensity rate (Figure 1). The non-singularity of the steady state infiltration rate can be explained by the microvariations of infiltration rate within the plot. Certain areas within the plot had infiltration rates less than the rainfall rate and runoff was generated. However, not all of the area was generating runoff and when the rainfall intensity was increased, these areas were still able to infiltrate more of the applied rainfall. Thus, the plot scale infiltration rate effectively increased. For the plot shown in Figure 1, the infiltration rate appears to increase by a factor of 3 - 5 x. Similar data were obtained from a number of landscape runoff plots. The data indicate that a single effective infiltration rate is not valid for this soil. The data also indicate a differential scaling effect depending on the tillage system. The no-till infiltration rate

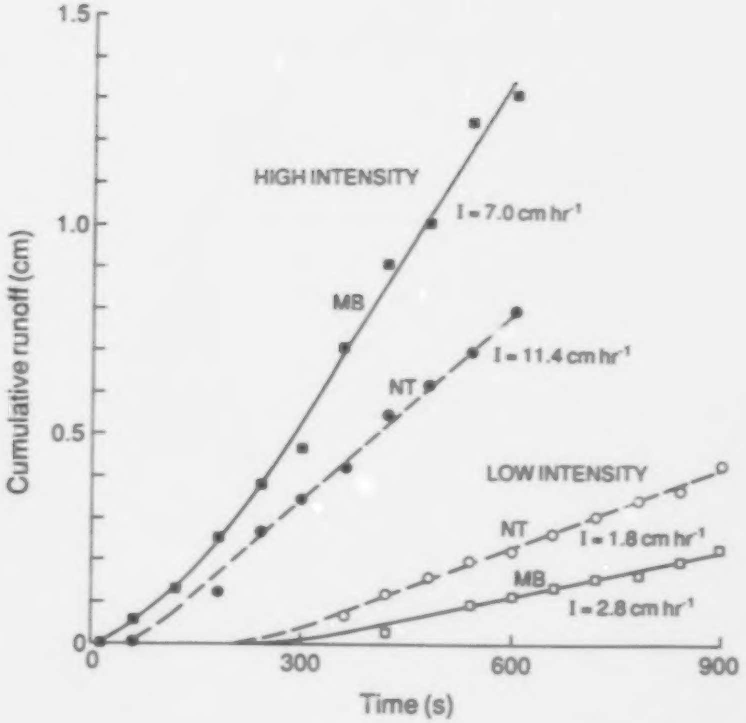

Figure 1: Runoff measurements for one tillage pair (MB = Moldboard, NT = Notill).

increased by 6 x when the rainfall rate increased, compared to a 2.5 x increase in the moldboard plough treatment. Measurements were also significantly affected by the size of the runoff plots which is discussed in more detail in the poster paper. The effect of changing the size of the plot is related to the spatial probability distribution of surface hydraulic properties.

The use of physically based models to predict soil loss and surface runoff assume that smaller scale heterogeneity can be lumped into effective parameter values. The data from this study support recent theoretical studies suggesting it may be difficult to define effective hydrologic variables that will adequately represent the behaviour of a heterogeneous hillslope. If this is true, then physical models based on effective (average) hillslope properties have limited practical predictive value. Stochastic methods of linking observation at different scales are being examined.

BP14

THE IMPACT OF CONTAMINANT EXPOSURE ON MUTATION RATES IN FISH: mtDNA VARIABILITY IN BROWN BULLHEADS (*Ictalurus nebulosus*) RESIDENT IN THE HURON-ERIE CORRIDOR.

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Increasing evidence (Varanasi 1989) indicates that benthic fishes may be exposed to very high levels of toxic contaminants, including polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) in their natural habitat. A number of studies (Baumann and Harshbarger 1985, Baumann et al. 1987, Baumann et al. 1989a, b, Black 1983, 1988) have shown high incidences of tumor formation in benthic fishes, primarily brown bullheads, which often inhabit highly contaminated habitats. These studies suggest that such bottom-dwelling fish may serve as sentinels for assessing the impact of contaminant exposure on both rates of malignant tumor formation, and induced mutation rates.

The purpose of the present study was to determine the utility of mitochondrial DNA (mtDNA) markers in assessing such mutational inputs by determining if there was any association between mtDNA diversity in the brown bullhead, *Ictalurus nebulosus*, and exposure to toxic contaminants. The PAHs in particular are known to preferentially bind to mtDNA (Backer et al. 1980) to induce mutations primarily by base substitutions (Eisenstadt et al. 1982). We chose to concentrate on a field survey of populations of *I. nebulosus*, which reside in both relatively pristine habitats and highly contaminated sites. A positive correlation between mtDNA clonal diversity and contaminant levels would suggest that mutation rates are a likely source of increased levels of diversity. The lack of such an association would indicate that mechanisms other than mutation (i.e. selection, founder effect) may be more important in influencing the population structure of this fish species.

Specimens of brown bullhead (*I. nebulosus*) were collected from five sites in the vicinity of the western basin of Lake Erie offshore from Leamington, Ontario (population A), Mitchell's Bay in Lake St. Clair (population B), and three tributaries which flow into Lake Erie, the Huron River (population C), Black River (population D), and Cuyahoga River, Ohio (population E). Based on data from the literature, estimates of contaminant levels in the sediments from each site were calculated. Both the Black (D) and Cuyahoga (E) River sites have elevated levels of heavy metals, and population E had very high levels of PCBs, when compared with the other sites. PAHs were also very high at sites D and E, and very low at site C; no PAH data are available from either sites A or B. A contaminant index for each site was calculated by first, ranking from highest level (1) to lowest level (5) each contaminant group found at a given site; i.e. comparable heavy metals, PCBs, PAHs. The mean value of these ranks was then calculated to represent a contaminant index for each site.

Live bullhead specimens from populations A and B were brought back to the lab and maintained for up to several weeks before being sacrificed. Liver specimens from freshly caught fish at sites C, D, and E were obtained from the U.S. Fish and Wildlife Service, Ann Arbor, Michigan, along with body length and body weight data for each specimen. Livers were processed for mitochondrial DNA (mtDNA) extraction within 72-hours of collection. Livers were kept on ice until processing was complete.

Mitochondrial DNA was isolated and purified from hepatic and gonadal tissues from individual fish following the protocols of Chapman and Powers (1984). The purified mtDNA was digested using hexanucleotide restriction endonucleases (i.e. six-base cutters) supplied by Bethesda Research Laboratories using recommended temperatures and buffer conditions as supplied by the manufacturer. Specimens from populations A and B were screened initially using 35 hexanucleotide restriction enzymes. Eleven enzymes were found to produce either no or a single restriction site, while eight enzymes showed more than one restriction site, but all profiles were monomorphic (same for all fish). The remaining 16 enzymes showed more than one restriction site, and were polymorphic for restriction fragment profiles. We therefore concentrated on using these 16 polymorphic enzymes for the analysis of all subsequent fish in populations C, D, and E.

Electrophoresis of DNA fragments was conducted using 0.8% and 1.2% horizontal agarose gels. Fragments were run into the gels for 30 minutes at 20 volts, and then run for an additional eight hours at 40-45 volts at room temperature. Upon completion of electrophoresis, gels were placed in staining trays containing 5 µg/ml of ethidium bromide (which intercalates into the DNA), and stained for 30 minutes on a shaking table. Gels were de-stained overnight in nanopure water, placed on an ultraviolet light box (wavelength 302 nm) in a dark room, and DNA fragments were visualized and photographed using a Polaroid MP-4 land camera. All gels were run with two lambda DNA standards, which had been digested using Eco-RV and Hind-III enzymes combined, and Hind-III alone.

Polymorphic restriction fragment patterns were coded with the restriction enzyme used and labelled alphabetically in the order of discovery (i.e. Dra-I "A", "B", etc.). If a monomorphic pattern was found using a given restriction enzyme, it was designated as the "A-type" pattern. A composite genotype for each fish could be constructed based on the restriction pattern at each enzyme. Fish that exhibited identical composite genotypes were considered members of the same mitochondrial clone.

A total of 20 unique mtDNA clones were found across all five populations. Seven of eight fish from population A showed unique mtDNA clonal types, while four of eight fish from population B were unique. Unfortunately, sample sizes for these two populations are small. However, data from population C indicated a total of 13 clones present out of 20 fish analyzed, while population D had three clones and population E had only two clones, based on sample sizes of 29 and 25 fish, respectively.

A more valid measurement of clonal diversity, which reduces sample size bias, is the effective number of clones in a population (Parker, 1979). Effective number of clones in a given population was calculated as the value 1/C (Simpson's measure of concentration $C = \sum p(i)$, where p is the frequency of the *i*th clone in the population, and the summation is over all clones; Parker, 1979). Population A had the highest (6.4) effective number of clones, with population C having a slightly lower value (5.2). In contrast, populations D and E had the lowest (1.3) and second lowest (1.6) values, respectively.

Of the 98 fish analyzed, two mtDNA clones were most abundant and constituted 79.6% (78/98) of the fish found in all five populations. Clone 1 represented 37.8% (37/98) of the fish surveyed, while clone 2 represented 41.8% (41/98) of all the fish analyzed. Of the 13 enzymes that were used in the final analysis, these two clones differed only at Dra-I, where a single fragment polymorphism was detected.

Non-parametric statistics using Kendall's (tau) rank correlation coefficient revealed a negative correlation (tau = - 0.316) between sediment contaminant level (measured as the contaminant index) and mtDNA clonal diversity (measured as the effective number of clones in a given population). However, this value was not significant (P = 0.4122).

Results from this study revealed relatively high levels of mtDNA clonal diversity (20 distinct mtDNA clones out of 98 fish) among populations of brown bullheads when compared with other species of fishes from the Great Lakes watershed. For example, Billington and Hebert (1988) observed a total of nine distinct mtDNA clones out of 141 specimens of walleye (*Stizostedion vitreum*) from across the Great Lakes watershed, while Grewe and Hebert (1988) identified 13 clones out of 151 specimens of lake trout (*Salvelinus namaycush*) from both hatchery and natural populations extending from Manitoba to upstate New York. Interestingly, the most diverse bullhead populations (A and C) were found in relatively "pristine" habitats. In comparison, two populations (D and E) from highly contaminated sites had very low levels of mtDNA clonal diversity. A broader geographic survey of additional brown bullhead populations needs to be conducted to determine macrogeographic patterns of mtDNA clonal diversity in this species. In addition, it would be useful to obtain additional data from other highly contaminated sites to see if the trends observed here are more robust. Presently, we are in the process of analyzing specimens from one other highly contaminated site, the Trenton Channel of the Detroit River.

These results suggest that mechanisms other than contaminant-induced mutations may be influencing levels of variability within the mtDNA genome of brown bullheads. Surveys of mtDNA variability in natural populations serve as a valuable first step in assessing potential impacts of contaminants, but used alone, such surveys have limited utility for assessing mutational inputs into the mtDNA genome. Viable mutations of mtDNA are most likely to be found in the non-coding control region of the mtDNA molecule. Indeed, this region is the most variable both within and between vertebrate species (Brown 1986). Direct sequence analysis of control segment nucleotides is a more sensitive method of detecting mutationally-derived variation between mtDNA clones than is hexanucleotide restriction site analysis. Currently, we are isolating mtDNA molecules from eggs of individual brown bullheads, which have been exposed naturally to high levels of mutagenic agents. Subsequently, these mtDNA molecules will be sequenced and analysed for variation in the control region. Coupled with field surveys, this more rigorous and sensitive method for detecting mtDNA variation should increase the probability of detecting mutational events due to contaminant exposure in aquatic organisms such as bottom-dwelling fish.

BP15

GEOCHEMICAL ASSOCIATIONS OF Cd, Cu, Pb, Zn, Fe AND Mn WITH SIZE FRACTIONATED SUSPENDED SEDIMENTS IN THE DON RIVER.

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The Don River drains a generally highly urbanized watershed of 376 km^2 and runs approximately 30 km through Metropolitan Toronto before discharging into Lake Ontario through the Keating Channel. There are over 1400 street run-off and industrial discharge outfalls on the river as well as a major sewage treatment plant and a snowmelt yard. Increasing problems with contaminated sediments in the Keating Channel and the Harbour have led to questions about sources of sediments and associated metal loads, development of in-place pollutants, relationships between sediment composition and water quality and whether in-place pollution and its effects on aquatic ecosystems can be predicted.

It has become increasingly evident that the ultimate fate, and therefore degree of in-place pollution and potential bioavailability of heavy metals is heavily dependent on their geochemical association with, and transport by, suspended sediments. We have been monitoring the geochemical associations (exchangeable, oxide associated, organic associated and residually associated) of Cd, Cu, Pb, Zn, Fe and Mn within the pool of total suspended particulates (bulk samples) over the last year in the Don River. In addition, we have collected size fractionated and subsequently geochemically fractionated suspended sediments at 3 sites, and begun limited work on stormwater runoff events.

To collect bulk suspended sediment samples, river water is pumped into acid washed polyethylene carboys using a *Little Giant* potent pump, with a polypropylene head. At each sampling time, depth is determined across the transect of the river channel at 1m intervals. Velocity is measured using a Gurley current meter at 2 -3 depths at each interval. These data are then used to compute discharge. Discharges are calibrated with MTRCA data for concurrent sites. Water samples are also taken for TDS and LOI analyses and particle size distribution. Particle size distribution is determined using a laser particle sizing system (Brinkmann Laser Particle Size Analyzer). In the lab, the collected water sample is emptied into an acid washed "bathtub", hooked up to a Sorval SS-34 centrifuge. Suspended sediments are collected from the water sample by continuous flow (12000 x g, flow rate of ~3 -5 minutes.L^{-1}) within 24 hours of water collection. Centrifuge discharge is collected and filtered through a 0.45 um filter to assure complete particulate removal.

Size fractionation of suspended sediments into 5 size classes is achieved using a wet sieving technique. Suspended sediments in the > 102um and the 63um - 102um size classes are collected in the field, by pumping river water through acid washed Nitex sieves. The filtrate from the 63um sieve is collected in carboys and brought back to the lab. This filtrate is then re-filtered through the 10um sieve and the filtrate collected. This filtrate is again re-filtered through a 5um sieve, that filtrate collected and re-filtered through a 1um sieve. Suspended sediment collected on the sieves are scraped and backwashed with deionized water into centrifuge tubes for subsequent chemical analyses.

All glassware, centrifuge tubes, vials and pipettes are acid washed in 10% HNO$_3$ and rinsed with deionized water 5 times prior to use. Once the suspended sediments have been isolated, they are divided into 3 replicates and placed in 50mL polyethylene centrifuge tubes. These samples are then run through a sequential extraction scheme to extract metals in the four operationally defined geochemical phases. Blanks and NBS standards are run with every set of samples to account for percent recovery and potential contamination. The supernatants from each extraction step are analyzed using flame atomic absorption (Laboratory Instruments, Model 351) for 6 metals (Cd, Cu, Pb, Zn, Fe, and Mn).

Centrifuge intake rate is critical. We have found that a flow rate of 3-5 minutes.L^{-1} is necessary in order to retain the entire suspended particle spectrum. In the absence of prior information on particle shape and density, we strongly recommend that centrifuge discharge be filtered and analysed to assure complete particle retention.

The bulk geochemical associations for the 6 metals follow 1 of 3 general patterns: (1.) concentration remains relatively constant across sampling sites and for different sampling times within a given site. Geochemical associations remain stable (*e.g.* Cd). (2.) concentrations increase in a downstream manner and geochemical associations shift (*e.g.* Cu and Fe). And (3.) concentrations and geochemical associations vary across sites and sampling times (*e.g.* Pb, Zn, and Mn).

Cd concentrations remain reasonably constant (range 0 - 20 ug.g^{-1}) along the system and are generally associated with the reducible, *i.e.* oxide, phase. These results are consistent with a hypothesis that the major source of Cd is geochemical, that it enters the system already associated with clay oxides (*i.e.* erosion) in the upper "reaches" of the Don and that there is no redistribution to other phases, despite changes in system chemical matrix.

In contrast, Cu concentrations increase from below 100 ug.g^{-1} at sites 1 and 2, to over 100 ug.g^{-1} at site 3, and closer to 200 ug.g^{-1} at site 4. Furthermore, whereas sites 1 and 2 show reasonably equal distributions of Cu between the oxidizable and residual phases, at sites 3 and 4, Cu is associated more with the oxidizable phase. These results are consistent with a hypothesis of increasing and anthropogenically associated loadings. These results raise the following questions, where is the Cu coming from, and what contributes to its redistribution?

In a similar fashion, Fe is relatively lower at sites 1 and 2 (below 50 mg.g^{-1}) compared with sites 3 and 4 (≥ 50 mg.g^{-1}). While Fe is associated predominantly with the reducible and the residual phases at all sites, residually associated Fe appears to be a larger percentage of the Fe pool by site 4.

Pb levels increase from sites 1 and 2 to site 3, but decrease again at site 4. At sites 1, 2, and 4 Pb concentrations range from 0 to 0.4 mg.g^{-1}. At site 3, Pb levels range from 0.4 to 1 mg.g^{-1}. Pb is associated predominantly with the reducible and residual phases at sites 1 and 2, but along the system towards sites 3 and 4, there appears to be a decrease in reducibly associated Pb while residually associated Pb is conserved.

Zn levels are low at site 1 (≤ 0.5mg.g^{-1}), variable at sites 2 and 3 (range 0.1 to 3 mg.g^{-1}), and fairly consistent at site 4 (≥ 0.6 mg.g^{-1}). For the most part, variance seems to be contributed by changes in the reducibly associated pool.

Mn decreases between sites 1 and 2 (from 2 - 5 mg.g^{-1} to ≤ 2 mg.g^{-1}), with a higher decrease in the reducible than any other phase. Substantial increases in reducible associated Mn enter at site 3 (total concentrations ranging between 3 - 6 mg.g^{-1}), and appear to have to have left again by site 4 (total concentrations ranging between 1 - 5 mg.g^{-1}).

To examine the relationships between sediment particle size, metal load and geochemical phase, we have size fractionated suspended sediment samples into 5 particulate sediment classes ((1) > 102um, (2) 63um < • < 102um, (3) 10um < • < 63um, (4) 5um < • < 10 um, (5) 1um < • < 5um), at 3 sites. Within each of these 5 size classes, the association of metals with 4 geochemical phases was determined. For all 6 metals, the highest concentrations were associated with the smallest size class. However, the 2nd highest concentration of Cu, Pb, Fe and Mn were found in the 3rd size class (10um < • < 63um). Cd results show a different pattern, with the 5um to 10um size fraction (4), having the 2nd highest concentration of metal associated with it. Zn concentrations are also bimodal with the 2nd peak in the >102um size class (1). Conventional wisdom suggests that smaller particles should have a higher concentration of metal associated with them due to differences in the relative potential for sorption onto clay mineral, hydrous oxide and organic matter surfaces, all of which tend to be concentrated in the smaller grain sizes. Our results indicating relatively higher concentrations of most metals in larger size classes compared to the 2nd smallest size class, and differences among metals as to which size class has the 2nd highest concentration, suggest deviations from the expected may be the result of differing antecedent metal ligand associations. Such deviations may be attributable to different source loadings of metals and/or ligands in the Don.

Despite the variable size particle–metal associated patterns outlined above, the highest proportion of residually associated metal is in the smallest size class. Thus, the smallest particles have a higher concentration of metal associated with them, and, within this size class there is a larger metal association with the residual phase. Some of the variance attendant with our bulk sampling is attributable to storm events and it has become obvious that stormwater runoff is a significant contributor of heavy metals. We have therefore begun to sample rain events in the Don. Our preliminary data show that stormwater runoff has elevated levels of metals associated with it (3 fold increases in metal concentration). Furthermore these metals are more associated with the more tightly bound ("residual") phase than with the more labile ("exchangeable") phase. In addition, there is a shift in particle size distribution to a greater proportion of smaller particles (baseflow concentrations of <63um suspended sediments were ~ 65 - 70%, after stormwater runoff into the river the proportion increased to ~ 90 - 97%), with lower organic content (baseflow organic content as measured by LOI was ~ 50%, but decreased following stormwater runoff to ~ 15-20%) It is obvious that a substantial portion of total metal loading is associated with short term storm events. Further, substantial changes in the nature of the dominant ligands and particles entering the system occur during rain events.

These results implicate the role of particle size in explaining variance in bulk data. The size fractionated results indicate higher concentrations of metal associated with the smallest suspended particles (1um - 5 um), and a higher proportion of residually associated metal in the smallest size class. Stormwater runoff had higher concentrations of metals associated with it, and further these metals were associated more with the residual phase. The particle size distribution of stormwater runoff indicated a much higher proportion of smaller particles in comparison with baseflow particle size distributions.

BP16

"ASSESSMENT OF THE BIOLOGICALLY-BASED LOW FLOW ANALYSIS TECHNIQUE"

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Background

The goal of the Ontario Ministry of the Environment (MOE), with respect to surface water quality management is "to ensure that the surface waters of the Province are of a quality which is satisfactory for aquatic life and recreation" (MOE, 1984). As part of its mandate, the MOE is responsible for reviewing and approving applications to allow industries and municipalities to discharge effluent into receiving water bodies. Part of the approval process involves an assessment of existing point and non-point sources of pollutants, and historical flow records to determine the study area's wasteload allocation (WLA). The present WLA methodology involves defining critical low flows using a hydrologically-based (extreme value analysis) design flow $7Q_{20}$ - the 7-day average low flow occurring once in 20 years. This is used as a measure of the waste assimilative capacity of receiving waters.

The historical justification for the selection of a design flow criterion in Ontario such as the $7Q_{20}$ flow is unknown. Typically, the parameters used in extreme value analysis are unrelated to biological, toxicological or ecological considerations. In selecting a design low flow, two important factors must be accounted for when assessing exposure conditions and setting water quality requirements: the duration of adverse exposure and the frequency with which water quality criteria are exceeded.

The United States Environmental Protection Agency's (US EPA) Office of Research and Development has developed, as part of its policy initiative, a biological and chemical assessment technique to control toxic pollution (US EPA, 1985). The technique incorporates a two-number aquatic life water quality criteria. The two-number WQC defines the duration and frequency of low flows and concentrations which may result in acute or chronic toxicity levels in aquatic life.

The two-number WQC are identified as:

1) A Criterion Continuous Concentration (CCC) of a pollutant occurring during a chronic design flow Q_{CCC}; and
2) a Criterion Maximum Concentration (CMC) of a pollutant occurring during an acute design flow Q_{CMC}.

The two criteria correspond to two flow-concentration conditions which may result in toxic effects to aquatic life. The CCC is a lower concentration of pollutant, but which occurs over a sufficient length of time to have toxic effects. The CMC corresponds to a high concentration of pollutant which only requires a short duration to have toxic effects on aquatic life.

The purpose of this research study is to analyse and compare the existing hydrologic methodology for defining low flows (extreme value analysis) to the biologically based methodology developed by the U.S. EPA.

Two objectives of this study are to 1) assess the practical usefulness of the U.S. EPA biologically-based method, and 2) to confirm the merit in continued use of $7Q_{20}$ and/or suggest an alternate xQy criteria which would be more consistent with the biologically defined flows.

Methodology

Streamflow data for 30 hydrometric stations in Ontario were assembled from the archives of the Water Survey of Canada. Daily average streamflow values were used in the analysis for determination of both the chronic and acute design flows.

To protect against acute effects the duration of adverse exposure must be set at as short a time period as practicable. The EPA recommends a one-hour averaging duration period for the Q_{CMC}. To protect against chronic effects the duration must be short enough to maintain the concentration at or below the CCC over the time period but long enough to allow some excursions above the CCC without detrimental effects on the aquatic community. From extensive chronic toxicity tests on single parameters as well as on whole effluents the U.S. EPA concluded that after four days impacts on aquatic test organisms began to occur.

The frequency at which an exceedence may occur is determined after examining the severity of the expected biological impact. The US EPA recommends that the one hour average should not exceed the CMC more than once in three years on average, and the four day average contribution should not exceed the CCC more than once every three years on average.

A literature review of existing toxicological research on aquatic life in Ontario river systems indicated that the frequency and magnitude of exposure to design criteria exceedences are dependent on the species present, their abundance, the number of refuge areas, etc. Until additional research and data are collected with regard to these factors, the information available in the literature review indicates the duration and frequency time periods specified by the EPA are also appropriate for river systems in Ontario.

The biologically-based design low flows (Q_{CCC} and Q_{CMC}) are determined by application of an empirical calculation method to a hydrometric data set. The calculation of the biologically based low flow uses the following five step process:

1) Calculation of the allowed number of excursions based on design criteria
2) Calculation of the X-day running averages of streamflow
3) Determination of the number of excursions of a specified flow in a set of running averages
4) Initiation of iterative computational procedure by defining initial limits of design flow and the initial seed trial flow

5) Iterative convergence of computations to the biologically-based design flow

A computer model entitled DFLOW (U.S. EPA, 1986) was modified to permit interactive and batch operations to determine biologically and hydrologically-based low flows for hydrometric data collected on Ontario rivers.

Evaluation Process

Recent studies carried out by MOE (Logan, 1986, 1988) focussed on evaluating the performance of six rivers in the Province of Ontario with respect to satisfying water quality objectives. The study used an evaluation process which considered probability concepts of reliability, resiliency and vulnerability. These concepts were applied in a general sense in evaluating and comparing the two low flow design methodologies.

The following three evaluation criteria were used in assessing the performance of the existing definition of low flow ($7Q_{20}$) and other hydrologically defined low flows ($1Q_{10}$, $3Q_{10}$, $1Q_{20}$, $3Q_{20}$, etc.) with respect to biological considerations:

1) the ratio of the number of excursions which would result if the hydrologic flow was used as the design criteria versus the number of excursions which would occur using the biologically defined flow as the design criteria.

2) the (absolute) difference in magnitude of design low flows using the two design low flow methodologies.

3) the (absolute) relative difference in magnitude of design low flows using the two design low flow methodologies.

A measure of the reliability of a hydrologically defined low flow which appropriately reflects biological considerations is a comparison which would result in a similar number of excursions as that occurring using the biologically based methodology. In addition, the average flow magnitudes should be similar.

The concept of resiliency, or the ability of a river system to recover from an excursion from water quality objectives, is implicit in the definition of the biologically based low flows. Therefore, a hydrologically defined low flow of similar magnitude to the Q_{CCC} and Q_{CMC} ensures resiliency.

Vulnerability, as defined by Logan, is a measure involving intensity and duration of exceedance of water quality objectives. This is used to assess the severity of a failure in a system. In the context of this study, the vulnerability of a river system was indexed in terms of the sensitivity of the number of excursions from water quality objectives to the biologically based design flow. In other words, vulnerability was assessed relative to the increased number of excursions as the hydrologic design low flow deviates from the biologically defined design low flow.

Results

The comparison of Q_{CCC} and Q_{CMC} design flows to hydrologically defined low flows indicated that the current design flow ($7Q_{20}$) is the most similar to the Q_{CCC} design flow in terms of flow magnitudes and the number of excursions, based on results for 30 hydrometric stations. (With respect to acute design flows, the optimum design low flow is either the $1Q_{20}$ or $3Q_{20}$.) Therefore, with respect to reliability, it can be concluded that the MOE is using an appropriate design criteria.

Figure 1 illustrates the concept of vulnerability with respect to the number of excursions which could occur if the Q_{CCC} design low flow was to deviate from its appropriate biologically defined value. The figure illustrates, for example, that if the design low flow was to deviate from the biological value by 25%, an excursion could be expected to occur once a year, on average, rather than the desired frequency of once every three years. Thus, a small difference in value of the design low flow could have a significant impact on the resiliency of the river system. Since the hydrologic $7Q_{20}$ is nearly equivalent in magnitude on average to the Q_{CCC}, the continued use of $7Q_{20}$ would maintain a high resiliency and a low vulnerability during low flow conditions for river systems in Ontario.

The findings of this study are generally consistent with the findings of a recent investigation (Logan, 1986) which concluded that the $7Q_{20}$ design low flow provides high reliability, moderate resiliency and negligible vulnerability.

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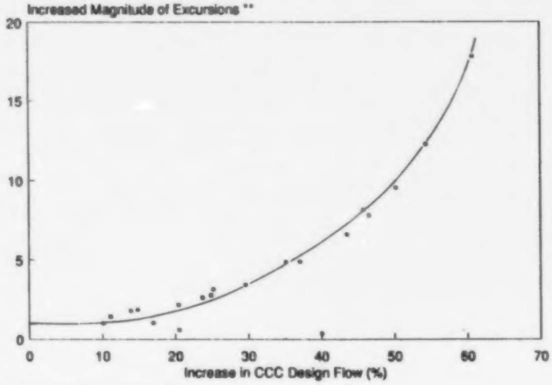
Vulnerability of River Systems



** Relative to CCC Excurs. Once in 3 Yrs

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FIGURE . 1

BP17

REGIONAL ANALYSIS OF LOW FLOW CHARACTERISTICS

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Ontario, M2H 2S5

The knowledge of hydrologic characteristics which exist during low flow conditions can be of primary importance for some watercourses. The identification of low flow characteristics within a watercourse is most easily accomplished using continuous hydrometric data recorded for the stream. However, this is limited to the availability of suitable long term discharge records at the location of interest. The objective of this investigation is to develop a practically oriented technique for estimating low flow characteristics at ungauged locations.

A pilot area was selected in Southern Ontario comprised of areas of the Southwestern and West Central regions of the Ministry of the Environment. Recent investigations by Cumming Cockburn Limited resulted in the analysis of all available hydrometric data series for Water Survey of Canada gauged stations within Ontario with suitable record. The results of this study were available to assist in the development of the prediction techniques. Relevant low flow statistics and other watershed characteristics were derived for 65 stream gauge locations in these areas.

Initially, a background review was undertaken to confirm the most appropriate single station and regionalization techniques. It was confirmed that the Gumbel III extreme value distribution generally has been found as the "best fitting" distribution for low flow data of various durations for analysis of single station records. However, other investigators have concluded that the Gumbel III distribution becomes unstable if the sample has a skewness of less than -1.08. Therefore, it was concluded that the Three Parameter Log Normal Distribution should be used as an alternate distribution for samples with large negative skewness.

Four alternative prediction methods were developed and evaluated; 1) Regression Equations, 2) Index method, 3) Mapping Proration, and 4) Isolines.

1) Regression Equations

The primary target of the prediction techniques was identified as the average 7 day consecutive low flow value with an average recurrence interval of once in 20 years. Other low flow characteristics examined were 3, 7, and 30 day consecutive low flows with recurrence intervals of 2, 20 and 50 years. In addition, a preliminary equation tc predict the flows which are equalled or exceeded 95 percent of the time was also developed.

The background review also confirmed the widespread use of statistical multiple linear regression techniques to regionalize low flow characteristics. It was also found that low flow characteristics depend largely on physiographic indices. On the basis of the literature review, it was decided to include the following parameters in the development of a data base for the Southwestern and West Central Regions of Southern Ontario: drainage area (DA), mean annual snowfall (MAS), mean annual precipitation (MAP), mean annual runoff (MAR), area controlled by lakes and swamps (ACLS), latitude (LAT), longitude (LONG), 10/85 slope (SLP), stream length (LEN), years of daily data (DYRS), and Base Flow Index (BFI).

2) Index Method

Regression results indicated that low flow characteristics are highly correlated to drainage area. Therefore, an index of low flow characteristics (i.e. $7Q_2$) was plotted against drainage area. In addition, ratios of various n day and y year recurrence intervals were also plotted. Therefore, given a station's drainage area, any average consecutive n day, y year recurrence flow for the station could be determined (one example is given in Figure 1).

3) Mapped Isolines

Other investigators have developed isoline maps of a base flow index (BFI). BFI was found to be highly correlated to low flow characteristics. Isolines of $7Q_{20}$ were mapped using the BFI map as a basis. Additional work is required to refine the mapping of low flow isolines.

4) Unit Low Flow Proration

It is presently common practice to use this technique to estimate low flows values at ungauged locations. Unit area low flows for selected low flow statistics at nearby gauges are averaged and then prorated to the site location using drainage area.

The alternative methods were then applied and evaluated for 10 test stations to confirm the usefulness in predicting low flow characteristics for ungauged watersheds.

In general, the results indicated that the best estimation technique was the Regression analysis. It was found that low flows can be predicted based on drainage area (DA), base flow index (BFI), and stream length (LEN). Table 1 summarizes the equation format, coefficients and resulting statistics. The regression equation has an R^2 of 0.96 and a standard error of 0.21 when predicting the primary target of $7Q_{20}$. This was found to be a significant improvement on the results reported for similar low flow regression studies.

The remaining techniques are ranked; isoline maps, index method, and area proration. The study results, therefore, indicate that the first three methods all resulted in some improved prediction compared to the existing method.

Part II of the study which has recently commenced is investigating the application of the techniques to the Central and Southeastern regions. Preliminary results indicate that some refinements of these prediction methods are required.

HS Belore

H. S. Belore

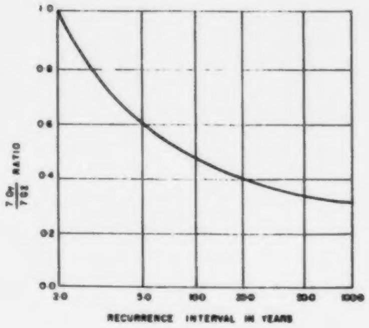
TABLE 1

Summary of Regression Analysis

Southwestern West Central Region

$$y = a_0 + a_1\,DA^3 + a_2\,BFI^2 + a_3\,LEN^2 + a_4\,LOG\,MAR + a_5\,LOG\,MAS$$

Dependent Parameter	Independent Parameters								
	a_0	a_1	a_2	a_3	a_4	a_5	N	SE	R^2
$7Q_2$	-.190	1.24×10^{-10}	1.67	8.35×10^{-5}			65	.31	.96
$7Q_{20}$	-.166	9.03×10^{-11}	1.10	4.67×10^{-5}			65	.21	.96
$7Q_{50}$	-.160	8.54×10^{-11}	1.02	3.92×10^{-5}			65	.21	.95
$3Q_2$	-.183	1.21×10^{-10}	1.55	7.81×10^{-5}			65	.28	.96
$3Q_{20}$	-.158	8.57×10^{-11}	.99	4.30×10^{-5}			65	.19	.96
$3Q_{50}$	-.150	7.92×10^{-11}	.91	3.64×10^{-5}			65	.19	.95
$30Q_2$	-.233	1.29×10^{-10}	2.12	1.12×10^{-4}			62	.41	.94
$30Q_{20}$	-.227	9.58×10^{-11}	1.52				62	.29	.94
$30Q_{50}$	-.078	1.25×10^{-10}	1.44				62	.33	.92
Q_{95}	-.230	1.26×10^{-10}	1.98	8.97×10^{-5}			65	.35	.95



7Q2 AS A FUNCTION OF DRAINAGE AREA
FOR SOUTHWESTERN WEST CENTRAL ONTARIO

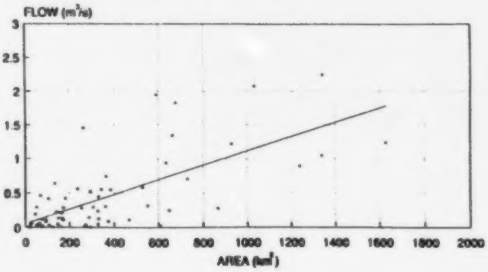


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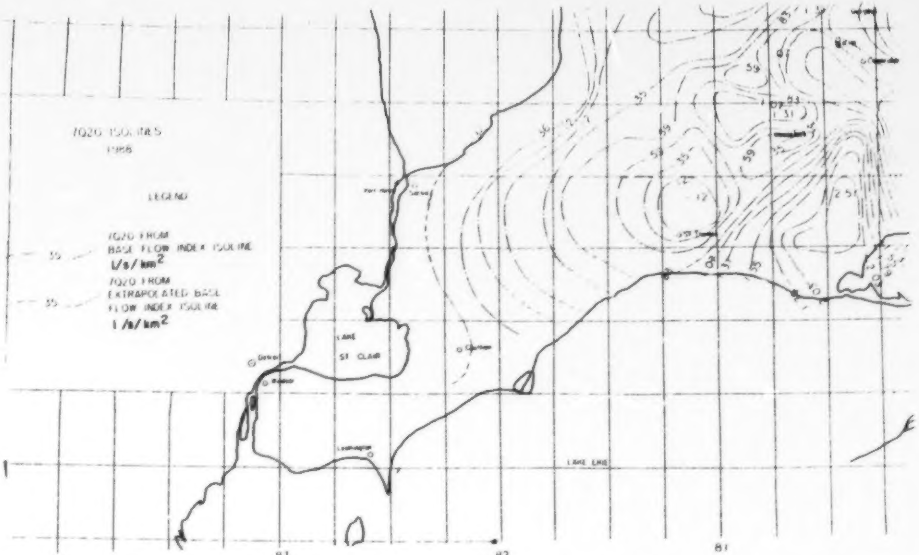
FIGURE 1


7Q20 ISOLINES
1988
LEGEND
55 7Q20 FROM BASE FLOW INDEX ISOLINE l/s/km²
55 7Q20 FROM EXTRAPOLATED BASE FLOW INDEX ISOLINE l/s/km²
LAKE ST CLAIR
LAKE ERIE
84
83
82
81

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7Q20 ISOLINE IN SOUTHWESTERN ONTARIO

FIGURE 2

BP18

Extended Abstract for PROJECT No. 392, Poster Presentation

MEASUREMENT OF CHEMICAL FLUXES FROM GROUNDWATER TO SURFACE WATER,

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Although recent work has shown that submerged discharge zones can be located (Lee 1985), it has been necessary to focus on both the large-scale (1 to 1000 m) and small-scale (0.01 to 1 m) in order to develop a methodology for measuring solute fluxes due to groundwater flow. Without site-specific data the impact of groundwater contamination on surface water bodies can rarely be predicted due to complex subsurface heterogeneity and chemical reactions. Computer simulations and an analysis of groundwater flow through the sediments of actual and hypothetical surface waters show that relatively thin layers of sediment (on the order of a few centimeters) may strongly influence migration paths and seepage flux distributions. We also note that when groundwater contaminants approach the sediment/water interface they enter an environment that is rich in natural, labile organic solids and is very bioactive. Denitrification, sulfate reduction, and degradation of organic contaminants are expected. Therefore the capability to locate discharge zones, to install piezometers and take samples within these zones is not expected to provide an adequate estimate of groundwater impact. These results have led us to measure directly solute fluxes in areas of contaminant discharge.

To test various sampling techniques for calculating mass fluxes based on pore water profiles, a seepage facility was set up in the laboratory. In the seepage facility, groundwater, flowing at a known flow rate through 1.2 m diameter tanks filled with sediment, discharged into a layer of overlying surface water. Pore-water profiles within the sediment were reproduced using groundwater and surface water of known chemistry.

Once steady-state flow was reached, chemical profiles for conservative and reactive constituents were measured using different techniques (peeper samples, cores and suction samples). Based on the observed profiles, the different components of the total mass flux (advective, diffusive and dispersive) were calculated for various solutes and the relative importance of each component were determined.

In the long term, it is intended to investigate which factors influence chemical profiles in areas of groundwater discharge with a special emphasis on the effect of the flow rate.

Lee, D., 1985. Journal of Hydrology 79:187-193

BP19

CARBON, SULFUR, AND NITROGEN CYCLING IN THREE UNCON. .. AQUIFER SYSTEMS IN ONTARIO.

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Institute for Groundwater Research, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, N2L 3G1.

Anthropogenic $SO_4^=$ and NO_3^- are increasingly common contaminants in shallow groundwaters in Ontario due to agricultural practices and acid rain deposition. In the absence of molecular oxygen, naturally occurring soluble organic carbon (DOC) is thought to be the electron donor in the natural microbial remediation of $SO_4^=$ and NO_3^- in groundwater. However, in order for microbes to be able to utilize DOC as an energy source to reduce NO_3^- or $SO_4^=$, the organic carbon source must be biologically available. Thus, natural bacterial remediation of NO_3^- or $SO_4^=$ may be controlled by the nature and flux of labile organic matter to the groundwater system.

Although in recent years much effort has been spent in the detection and remediation of man-made organic contaminants in groundwater, very little is actually known about the sources, geochemistry, and role of naturally occurring, soluble organic matter in groundwater.

The objective of this research is to evaluate the origin, fluxes, and geochemistry of soluble organic matter in three shallow sand aquifers in Ontario, as well as evaluate the role of naturally occurring soluble organic matter in microbially mediated redox processes that affect the various carbon, sulfur and nitrogen pools. The research will attempt to characterize and describe the geochemical evolution of fractions of soluble organic matter that form part of the DOC along the flow paths of several shallow aquifers. Evaluation of the age, origin and residence time of DOC in groundwater will be assessed using ^{14}C analyses.

Methods used are liquid chromatography, molecular sieving, stable isotopic mass spectrometry, gas chromatography / mass spectrometry (GC-MS), and Tandem Accelerator Mass Spectrometry (TAMS).

The three shallow sand aquifers studied are located near Rodney, Alliston, and Sturgeon Falls, Ontario. These sandy aquifers are contaminated with significant concentrations of NO_3^- (0-100 mg/L) and/or $SO_4^=$ (0-150 mg/L). The Rodney and Sturgeon Falls sites have shallow vadose less than ≈ 1 m thickness, whereas, the Alliston site has a thicker vadose zone of ≈ 4-5 m. Based on $\delta^{34}S$ analyses of aqueous sulfate, we concluded that $SO_4^=$ at Sturgeon Falls and Alliston is derived from acid rain deposition, whereas at Rodney additional $SO_4^=$ is derived from oxidation of organic bound and/or mineral sulfur. The nitrate is at Rodney and Alliston is derived from fertilizers and agricultural practices. Bacterial remediation of NO_3^- and/or $SO_4^=$ occurs at Rodney and Sturgeon Falls but not at Alliston.

Our data shows that high molecular weight (HMW) soluble organic matter at Rodney is rapidly flushed to the groundwater during recharge from the upper few centimeters of the soil profile in less than 2 years. The HMW DOC is composed of a mixture of old and young carbon, having a mean residence time of about 600 years. Low molecular weight DOC has ages similar to the aquifer kerogen, suggesting a link between the aqueous and solid organic carbon pools.

In the Sturgeon Falls aquifer HMW DOC entering the groundwater contains "post-bomb" ^{14}C, indicating soluble organic matter has residence times of less than about 30 years, and is recharged to the system in less than 1-2 years. Our data also indicate labile organic carbon may also be produced by fermenting bacteria acting on kerogen indigenous to the aquifer material.

At the Alliston site, however, a long residence time for soluble organic matter in the vadose zone is postulated due to a thick unsaturated zone, resulting in refractory, non-labile DOC reaching the groundwater. Results and interpretation of data from the Alliston site and 1989 summer field season will also be presented.

Current Research

Completion of field research and data analysis will comprise the final year of this project (1989-90). Our immediate goals are;

1. to complete detailed geochemical characterization of dissolved humic substances from all three sites,
2. to present a cognitive model for the origin and age of natural organic solutes in the three groundwater regimes, and,
3. to present a quantitative geochemical model for the evolution and mass transfer of natural DOC in groundwater flow systems.

BP20

MERCURY AND PCBS IN FISH USED AS A MAJOR FOOD SOURCE BY NORTHWESTERN ONTARIO NATIVE PEOPLES.

A.F. Johnson, A.L. Vaillancourt and C.M. Cox, Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario, M4V 1P5.

Abstract

As a result of the discovery of elevated PCB levels in the blood of native people living in isolated Northern communities, extensive surveys of the contaminants in fish from Big Trout Lake and Weagamow (Round) Lake - area lakes were undertaken in 1988. Analysis of 800 fish for mercury, PCBs and organochlorine pesticides revealed that fish were only a minor potential contributor of PCB's to the human diet. Certain species and sizes of fish were an important source of mercury to the diet. The results indicate the need for careful assessment and additional research on the dietary pathways of contaminants which may affect human populations.

Report

Figures 1 to 5 show the best-fit mercury versus fish length regressions for Walleye, Northern Pike and Lake Trout collected from the studied lakes. Larger specimens of these species were found to exceed the 0.2 ppm Federal Health & Welfare Canada guideline for maximum mercury concentration in fish consumed by those for whom fish is the basic source of protein in the diet. Figure 6 indicates that some individuals showed slightly elevated blood mercury levels, likely as a result of heavy fish consumption.

Figure 7 presents the Health & Welfare Canada data which prompted the analysis of large numbers of sport fish. It had been at first assumed that fish, a staple of the diet, would be high in PCBs.

Figure 8 shows that fish of several species, and even the carcass of Lake Trout were very low in PCBs. Tern's eggs (apparently consumed seasonally by some residents) and the Common Loon and Red Breasted Merganser (Fish Duck), which are also eaten, are very high in PCBs. Figure 9 indicates that single 117 gram meals of Tern's eggs, Loon meat or Fish Duck meat would provide a dose of PCBs to the consumer in excess of the Tolerable Daily Intake of PCBs of 1 microgram per kilogram body weight established by Health & Welfare Canada. Fish would provide only a small fraction of the Tolerable Daily intake of PCBs permitted.

Figure 1

HG in Big Trout Lake Walleye

Calculated Best-Fit Curves

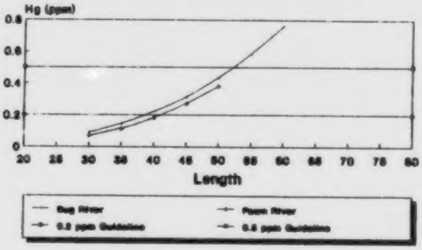


Figure 2

HG in Big Trout Lake N. Pike

Calculated Best-Fit Curves

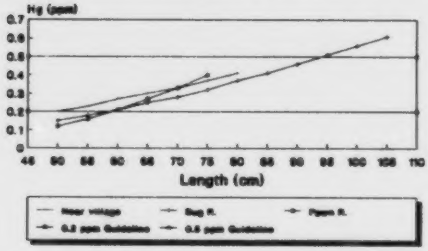


Figure 3

HG in Big Trout L. Lake Trout

Calculated Best-Fit Curves

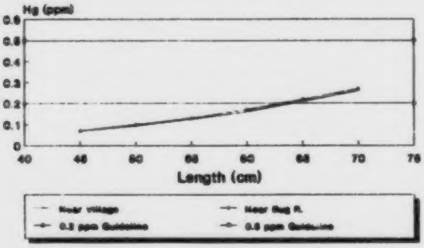
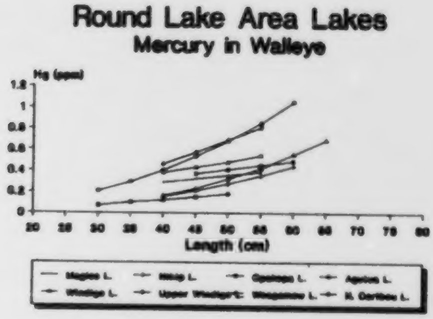
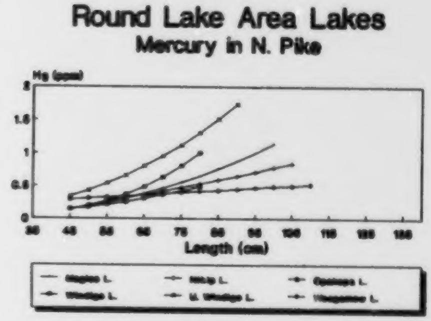


Figure 4



0.2 ppm Hg limit for high fish consumers

Figure 5



0.2 ppm Hg limit for high fish consumers

Figure 6

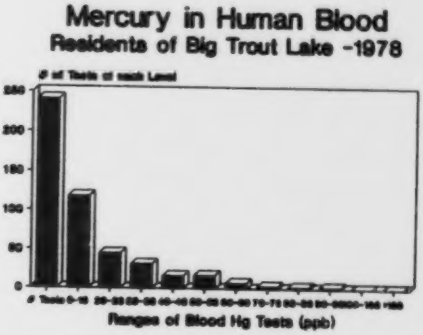
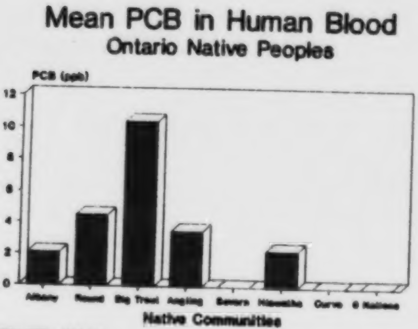


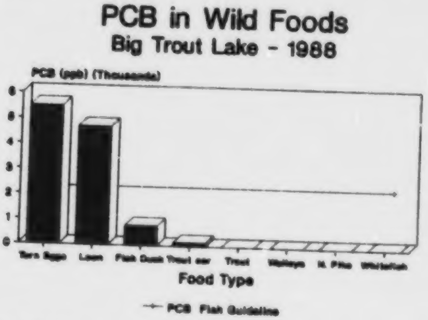
Figure 7



Mean PCB in Human Blood
Ontario Native Peoples

Arochlor 1260 - H&W Can.

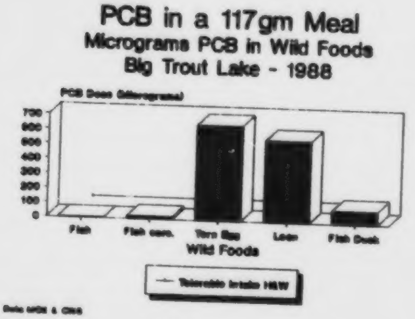
Figure 8



PCB in Wild Foods
Big Trout Lake - 1988

Data - MOE & CWS

Figure 9



PCB in a 117gm Meal
Micrograms PCB in Wild Foods
Big Trout Lake - 1988

Data MOE & CWS

BP21

A STUDY OF THE EFFECTIVENESS OF ONTARIO'S SPORT FISH CONSUMPTION GUIDELINES.

C.M. Cox*, A.L. Vaillancourt and A.F. Johnson, Water Resources Branch, Environment Ontario, Toronto, Ontario M4V 1P5

1. Introduction

Since 1977, the province of Ontario, through the Sport Fish Contaminant Monitoring Program, has distributed an annually-updated advisory publication on the suitability for consumption of Ontario sport fish. The 1989 "Guide to Eating Ontario Sport Fish" presently lists size-specific consumption advice, based on contaminant levels, for sport fish from over 1600 locations across Ontario.

In conjunction with the "Guide", questionnaire surveys have been included in 1978, 1983, 1986, and 1989. These questionnaires are used to determine the use and effectiveness of the "Guide", as well as Ontario anglers' fishing and sport fish consumption patterns.

In 1989, additional surveys are being conducted specifically for Great Lakes salmon and trout anglers, as they are potentially "higher risk" consumers than the average Ontario angler(from the "Guide" surveys) who consumes a variety of fish species (mainly warm-water species such as walleye) usually from inland locations. The potentially higher levels of risk are due to the elevated organic contaminant levels in Great Lakes salmon and trout (especially PCBs and mirex in Lake Ontario species). A comparison of the consumption patterns and "Guide" usage can be made between the two groups. There is a continuing need to determine the effectiveness of the "Guide" in providing contaminant information and consumption guidelines to all anglers. As well, there may be anglers who are either ignoring the guidelines or are unaware of them, and these anglers might be consuming fish at levels which may place them at a higher risk.

2. Methodology

The 1989 "Guide" questionnaire was enclosed in the "Guide" books. The 1989 Great Lakes surveys are being conducted using mailing lists derived from randomly selected entry forms for various Great Lakes salmon and trout derbies. The derbies involved in these surveys are the: Toronto Star Great Salmon Hunt (Lake Ontario), Chantry Chinook Classic (Lake Huron), Owen Sound Salmon Spectacular (Georgian Bay) and Michipicoten Salmon Derby (Lake Superior).

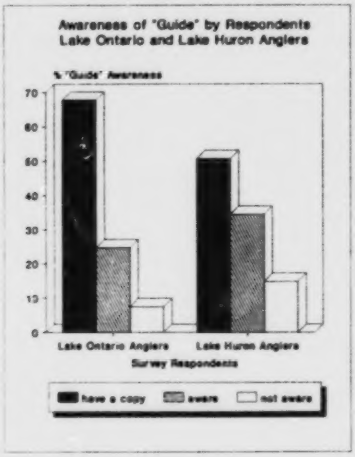
The questions were standard for all the Great Lakes surveys, and the consumption questions were comparable to those in the 1989 "Guide" survey. Comparisons could be made between anglers consuming salmon and trout from Lake Ontario (which have the highest organic contaminant levels and therefore more consumption restrictions) and from some of the other Great Lakes (where contaminant levels were much lower and fish were most frequently in the unlimited consumption category). Determinations could be made to see if anglers were aware of the "Guide", and if the "Guide" advice was being followed, based on the consumption patterns. If the advice was being followed, then anglers consuming Lake Ontario salmon and trout should eat less fish than both salmon and trout anglers fishing other Great Lakes, and the average Ontario angler fishing for a variety of species.

3. Results

The Lake Ontario and Lake Huron surveys have been completed, while, because of their late summer derby dates, the Georgian Bay and Lake Superior surveys have not yet been completed. As well, the 1989 "Guide" surveys are still being received, but over 800 responses have been used in the calculation of this survey's results.

Based on the Lake Ontario and Lake Huron surveys, there is a high awareness and usage of the "Guide" among anglers (see Figure 1).

Figure 1.



The question was asked if anglers who used the "Guide" followed the consumption guidelines, and 81% and 71% respectively of the Lake Ontario and Lake Huron anglers indicated that they did follow the guidelines. The guidelines for consuming fish with restrictions due to organic contaminants is a meal every two weeks for the long-term consumer (except for women of childbearing age and children under 15, who should not consume these fish at all). The frequency of consumption can be used as an indication of adherence to the "Guide" consumption guidelines. For Lake Ontario, where most of the salmon and trout are restricted, only 11.1% of the respondents consumed fish at a frequency greater than once every two weeks. For Lake Huron, where the salmon and trout are generally not restricted, 26.7% consumed these fish more frequently than once every two weeks, while for the "Guide" anglers, 18.0% consumed sport fish more frequently than this frequency.

The average daily sport fish consumption, which was derived from the meal size and meal frequency, was found to be the lowest for Lake Ontario anglers and the highest for Lake Huron anglers (see Figure 2). Figure 3 shows a comparison of the meal sizes consumed by "Guide", Lake Ontario and Lake Huron anglers. While the majority of anglers in all three surveys are consuming sport fish in meal sizes of 227 gm (8 oz) or less, there are fewer Lake Ontario respondents than other respondents consuming sport fish meals above 227 gm. As well, more than twice as many Lake Ontario anglers do not consume their catch (often because of an indicated concern about the contaminant levels).

Figure 2.

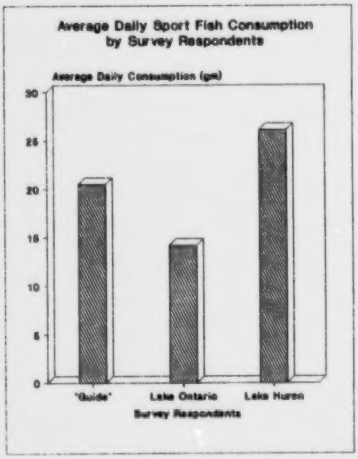
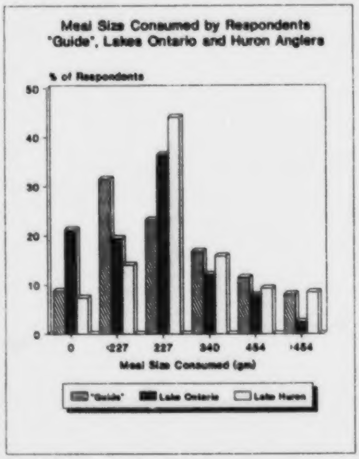


Figure 3.



As well, for the Great Lakes surveys, anglers were asked if they would keep a lake trout for consumption. Since lake trout normally have the highest organic contaminant levels found in the edible portion of salmon and trout, they are therefore most likely to be in the restricted consumption category. Lake Ontario anglers would be aware of this through the "Guide" information, and only 13.9% of the respondents indicated that they would keep a lake trout. In contrast, 94.4% of the Lake Huron anglers indicated that they would consume lake trout, as Lake Huron lake trout have much lower contaminant levels, and are frequently not restricted for consumption. Again, this would indicate an observance of the information in the "Guide".

4. Conclusions

1. The "Guide to Eating Ontario Sport Fish" is an effective means of conveying sport fish consumption advice to anglers.

2. The majority of anglers surveyed not only were aware of the "Guide", but had a copy.

3. The majority of anglers using the "Guide" were following the consumption guidelines.

4. Comparisons of consumption patterns through various surveys indicated that when consumption advice is more restrictive (eg. for Lake Ontario salmon and trout), anglers are consuming less fish. Conversely, when the guidelines indicate no consumption restrictions, anglers are consuming more fish.

5. Recommendation

Follow up medical studies could be done using surveys such as this, to focus on heavy fish consumers (eg. Lake Ontario salmon and trout anglers consuming fish much more frequently than the guidelines suggest), although few respondents were found in this category. Blood or hair samples may be used to determine if elevated levels of organic contaminants or mercury (in the case of anglers consuming large amounts of larger predator fish uch as walleye, which may have high mercury levels) are detected.

BP22

Sediment Bioassay Development : Addressing the Pros and Cons

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Windsor, Ontario N9B 3P4

The effects of sediment upon biota were measured in a variety of chronic bioassays. The purpose of this research was to develop a standardized solid-phase sediment bioassay using mayfly nymphs, chironomid larvae and juvenile fathead minnows.

Areas of concern include the impact of indigenous bulk chemistry of the sediment (ie. organic content, particle size composition), upon organism sublethal responses. The importance of life history characteristics (ie. life cycle stage, nutritional needs, ease of culturing) and ecological requirements (ie. habitat suitability, niche representation) will be highlighted throughout this paper.

The basic experimental system consisted of static, individual 2L widemouth glass jars containing 325mL of pre-sieved test sediment. Dechlorinated water was added to provide a 4:1 ratio (water:sediment) and allowed to settle overnight. Jars were randomly placed into a water bath. During the day of the test, the jars were aerated for at least one hour and the organisms were introduced in increments.

A total of 15 chironomid larvae or 10 mayfly nymphs or fathead minnows were added per jar. Each treatment consisted of three replicates. Prior to the bioassay, a random sub-sample of test animals were collected, weighed and measured. Measurements of wet weight, standard length and head capsule width were made upon individual animals at the termination of the test. Data is expressed as the mean of the means for the indicated number of replicates and the associated standard deviation.

Hexagenia mayfly nymphs

Burrowing mayflies are benthic invertebrates that dwell within U-shaped burrows formed within the sediment. Nymphs ingest detritus, organic matter and fine sediment particles.

The importance of the test duration and substrate characteristics upon nymphal growth was examined using uncontaminated sediments. Four month old cultured nymphs (avc. wt. 20.1mg ± 4.1) were exposed to five substrates ranging from sandy sediment to fine silt/clay material and rich, soft organic mud. After a period of 10 days, no significant change in weight was noticed across all sediment types (22.0mg ± 2.6, n=15). Increase in biomass became apparant within 21 days (33.8mg ± 7.6, n=15). High survivorship and increased growth was independent of sediment bulk chemistry and illustrates the suitability of young mayfly nymphs for the testing of a variety of sediments for sublethal effects.

In a separate experiment, the effect of feeding upon the growth and survival of Hexagenia was performed in a 21 day bioassay. Three month old nymphs (ave. wt. 8.77mg ± 1.0), were introduced into jars containing a clean control sediment and moderately contaminated sediments from St. Marys River and Grand River. All the sediments were predominately silt/clay in composition.

The diets included a solution of Tetra-fin and a combination of a Tetra-fin and Cerophyll. The treatments included an unfed group and high and low concentrations of each prepared diet.

Growth effects were similar for each type of diet and concentration. The trend was common to each test sediment. Even the weights of the unfed animals were comparable to those animals receiving a diet. A strong correlation was evident between percent mortality and nymphal growth for each sediment type. The lowest mortality was associated with Grand River sediments (0.66% ± 2.5, n=15), followed by the Control (5.33% ± 9.9, n=15) and St. Marys sediment exhibited the highest mortality (24.0% ± 18.8, n=15). After 21 days, nymphs from Grand River exposures grew 4-fold relative to the pre-exposed animals (32.1mg ± 4.3, n=15) while organisms in the control doubled in weight (21.4mg ± 6.3, n=15) and animals in the St. Marys experienced no growth (10.4mg ±1.6, n=15).

Young nymphs were capable of receiving adequate nutrients directly from the substrate and experienced no adverse stress or starvation due to the lack of feeding over a 21 day period. The differences in growth among the test sediments may be a result of both the differences in contaminant loadings and the amount of organic matter present.

Overall, immature mayfly nymphs are useful for measuring chronic endpoints and are tolerant of a range of sediment types. Mayfies are easily cultured and maintained in the laboratory and the eggs are readily stored. Because of the benthic nature of the mayfly, little or no feeding is required in a 21 day bioassay. Further studies are being conducted with older nymphs in order to determine the most sensitive life cycle stage adequate for chronic testing.

Chironomus midge larvae

Chironomid larvae are tube-dwellers that live near the sediment-water interface. The larvae are seston grazers and filter food particles from the overlying water. The entire life cycle is completed within 28-30 days, at which time adult emergence and mating occurs.

A partial life-cycle bioassay was performed in order to determine the extent habitat type effects larval survivorship, growth and development. 10 day old, 2nd instar cultured midge larvae were placed into jars holding five uncontaminated sediments and the test ran for a duration of 10 days. The organisms were fed a similar diet and experienced high survivorship across all sediment classes.

The best performance in terms of weight gain occurred upon the sandier substrates, Sed A (10.0mg ± 0.0, n=3) and Sed B (8.12mg ± 0.0, n=3). Growth was lower among the softer, fine-grained substrates, Sed C (7.02mg ± 0.0, n=3), Sed D (7.13mg ± 0.0, n=3) and Sed E (6.71mg ± 0.0, n=3). The larvae were all in the 4rth instar at the termination of the test. The sandy sediments may have contributed a better selection of material for the formation of tubes which may indirectly caused enhanced growth.

Chironomid larval growth was studied using sediment collected from three contaminated sites, St. Marys River (silt/clay), Toronto STP A (54% sand, 2.4% LOI), Toronto STP B (43% sand, 3.9% LOI) and clean sediment collected from Honey Harbor served as the control.

Half of the animals were not fed and suffered high mortality and no growth. The remaining animals received a diet of Tetra-fin and showed obvious growth effects. Inhibited growth occurred in the St. Marys exposures (3.63mg ± 1.0, n=3) and the greatest growth occurred for Toronto STP B (12.45mg ± 1.0, n=3). Similar results were obtained for Honey Harbor (9.59mg ± 1.0, n=3) and Toronto STP A (8.30mg ± 1.0, n=3).

Habitat suitability was the primary regulator of growth as indicated by the greater biomass obtained by the larvae introduced to the coarse-grained sediment, even though it possessed higher contaminant concentrations than the control.

Adult emergence was examined using similar test sediments as for the larval growth bioassay and allowed for the direct comparison between the two endpoints. The unfed treatments yielded no emergence of adults due to the lack of larval development. The mixed results for the fed animals did not correspond to the outcome of the larval growth experiment. Toronto STP B produced the highest percentage of emergence (71.5% ± 18.7, n=3) and Honey Harbor the lowest (46.5% ± 3.6, n=3). Moderate emergence occurred for St. Marys River (61.9% ± 10.4, n=3) and Toronto STP A (52.7% ± 36.0, n=3). The time to first emergence ranged from 17 to 22 days and lasted for a period of 6 to 7 days.

The influence of diet quality and quantity upon chironomid larval growth over a 10 day duration was conducted using sediments sampled from Canagagigue River, Toronto STP and a control.

The feeding treatments included Tetra-fin and a 60:40 mixture of Cerophyll and Tetra-fin. Both diets were allocated in high and low concentrations. The best growth arose using the Cerophyll-Tetra mixture. The higher concentration resulted in twice the amount of growth than the lower concentration for both diets. For instance, animals receiving the higher concentration of Cerophyll-Tetra in the jars containing Canagagique sediment had an average wet weight of 12.49mg ± 0.0 (n=3), Toronto STP, 10.92mg ± 0.0 (n=3) and for Honey Harbor, 9.54mg ± 0.0 (n=3). At the lower concentrations the following weights were measured: Canagagique River (6.40mg ± 1.0, n=3), Toronto

STP (5.99mg ± 0.0, n=3), Honey Harbor (6.40mg ± 1.0, n=3). Mortality across all treatments was 11.44% ± 7.4 (n=12).

The outcome of these experiments suggest chironomids serve as adequate organisms for chronic, sublethal bioassays. Multiple endpoints may be obtained from a genetically similar population. Larval growth can be measured over a short 10-12 day exposure and low variability in the data is expressed. Adult emergence is more variable but the experimental design was suitable for examining emergence within a 17-20 day period. Chironomids are easily cultured and capable of supplying a large number of offspring that may be used for several concurrent bioassays. The need for a proper diet during the bioassay may be considered a drawback and habitat preference appears to play a role.

Pimephales promelas minnow larvae

Juvenile fathead minnows are water-column dwellers and obtain food directly from the water or ingest food particles on the sediment surface.

The purpose of the following experiment was to study the effect of the lack of feeding upon stress that may develop in a 21 day sublethal bioassay. The initial average wet weight of the minnows was 216mg + 20. The minnows were exposed to five uncontaminated sediments of varying particle size composition and percent organic matter. The final weight averaged for all test sediments was 182mg ± 24 (n=15). The lack of larval growth may be due to the short duration of the test and the inability of fathead minnows to obtain any substantial food from the sediment. Therefore, minnows may be a poor indicator organism of growth even though high survivorship was maintained.

A further study was carried out to compare the use of different food sources that may serve as an appropriate diet during a bioassay. The diets included daphnia, 24-48h old brine shrimp, frozen brine shrimp and Tetra-fin. The animals were fed once or twice a day depending upon the treatment.

After 21 days the unfed animals (158mg ± 5, n=3) experienced no change in weight relative to the pre-exposed minnows (178mg ± 75). Those animals fed twice a day a diet of Tetra-fin (237mg ± 17, n=3) and live brine shrimp (222mg ± 13, n=3), exhibited improved growth over the unfed group. Animals fed Daphnia and frozen brine shrimp yielded small weight gains. The frequency of feeding did not have a strong impact upon growth.

It appears feeding is an important factor when considering the use of fathead minnows in a long term bioassay for the purpose of testing growth responses. Further studies will be carried out using other size classes which may improve upon the development of the sediment bioassay.